UNITED STATES
DEPARTMENT OF THE INTERIOR

AN ENGINEERING EVALUATION OF THE LONG-TUBE VERTICAL FALLING-FILM DISTILLATION PROCESS

OFFICE OF SALINE WATER
RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 139

UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

Kenneth Holum, Assistant Secretary
for Water and Power Development

AN ENGINEERING EVALUATION OF THE LONG-TUBE VERTICAL FALLING-FILM DISTILLATION PROCESS

By
The Dow Chemical Company

For
OFFICE OF SALINE WATER
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February 1965

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 Price $2.00

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FOREWARD

This is another of a series of reports designed to present accounts of progress on saline water conversion with the expectation that the exchange of such data will contribute to the long range development of economical processes applicable to large scale, low cost demineralization plants of multi-million gallon per day capacity for conversion of sea and other saline waters.

Except for minor editing, the data herein are as contained in a report submitted by The Dow Chemical Company, under Contract No. 14-01-0001-397. Neither the Department of the Interior nor any person acting on behalf of the Department, makes any warranty or presentation with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information or process equipment disclosed in this report may not infringe privately owned rights.

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SECTION I. INTRODUCTION

The saline-water conversion program was begun in 1952 with the purpose of developing a practical low-cost means of producing water, of suitable quality for municipal, industrial, and other beneficial uses, from saline water. The Office of Saline Water has developed conversion processes through research grants and contracts.

By Public Law 85-883, the Office of Saline Water was authorized to construct and operate not less than five saline-water-conversion demonstration plants for the production, from sea water or brackish water, of water for industrial, municipal, and other beneficial uses. The first of these demonstration plants to be built was a long-tube, vertical, falling-film, multiple-effect distillation plant at Freeport, Texas.

The long-tube, vertical evaporator design was first suggested by W. L. Badger and Associates. In 1957, a 2000-gallon-per-day pilot plant was erected. As a result of the pilot-plant test work, a 12-effect evaporator saline-water conversion plant was designed by W. L. Badger and Associates and constructed by Chicago Bridge and Iron. Since June 6, 1961, the Freeport plant has been operated by Stearns-Roger Corporation of Denver, Colorado. The plant has successfully operated for three years.

The Office of Saline Water requested an engineering evaluation of the long-tube, vertical, falling-film distillation process in order to use the operational knowledge to advance the science and technology of saline-water conversion and to contribute materially to low-cost desalination by increasing operational reliability and production of the long-tube, vertical, falling-film process.

It is the objective of this report to study the falling-film distillation and to prepare an engineering evaluation of the process and the design of major items of equipment, with particular emphasis upon improving production and operational reliability and upon reducing product cost.

SECTION II. SUMMARY AND CONCLUSIONS

A. Summary

An engineering evaluation of the OSW Demonstration Plant No. 1 has been completed. Heat and material balances for three sets of operating conditions were calculated. The intake complex was evaluated. The preheaters and cross exchangers were evaluated for the present operation and designed for two other operations.

An extensive study of the deaerator and its operation was carried out including sampling and chemical analysis. The evaporator design was evaluated for varying tube sizes and brine recirculation rates under three sets of conditions. The entrainment-separator design was evaluated for the present operation, and a study was made on the use of wire mist eliminators.

The materials of construction and corrosion problems of the plant were studied, samples examined, and radio logs taken. The pumps and other mechanical equipment were studied with emphasis on the more severe operating conditions proposed. The plant instrumentation was reviewed and evaluated.

A review of location and procedures for chemical sampling and analysis was made. The acid and caustic treatment of the sea water feed was reviewed and evaluated.

Through a literature survey, correct solubility limits for calcium sulfate scales were calculated and the scaling limits for the LTV plant determined. Ion-exchange softening for feed pretreatment was studied, and softening units were designed for plant operation at 275°F and 4:1 brine concentration, and at 300°F and 5:1 brine concentration. Application of the calcium-sulfate slurry process for feed water treatment to the LTV plant was extensively studied.

Treatment of the product water was studied, and the effect of the product water on the materials of construction was evaluated. Test spools and plant piping were examined and the corrosion evaluated. The effect of mixing product water with Freeport city water was studied. A normalized plant to produce one million gallons per day was designed and the economics determined.

B. Conclusions

The major conclusions from this study are:

1. Economic evaluation of the present plant operation and the two revised plant operations, Table II-I, indicate that the most economical process is the operation of the plant at an Effect I temperature of 300°F with ion-exchange softening of the sea water feed.

2. Using all of the process improvements determined in the engineering evaluation, a normalized, one-million-gallon-per-day plant was designed at a capital cost of $1,518,570 which would operate for $1.16 per thousand gallons.

3. A systematic study of the solubilities of calcium sulfate and a review of the scaling in the LTV plant have led to the conclusion that the first-effect temperature should not exceed 240°F to prevent $CaSO_4$ (anhydrite) formation, and that the last-effect concentration factor should not exceed three times normal sea water to prevent $CaSO_4 \cdot 2H_2O$ (gypsum) formation.

4. Removal of 50 per cent of the calcium by ion-exchange softening in a fluidized bed and regeneration with a concentrated brine will allow operating at 275°F in the first effect and a concentration factor of four times normal sea water in the last effect.

5. Removal of 65 per cent of the calcium will allow operation at 300°F in the first effect and a concentration factor of nearly five times normal sea water in the last effect.

6. Adaptation of the Badger anhydrite-seeding process to the present plant to permit 300°F operation is economically attractive provided a pre-Effect I hydraulic-cyclone seed recovery of 98 per cent can be achieved, and provided the feed sea water can be heated to 300°F without scaling.

7. The existing deaerator is adequate in size and design to maintain the total CO_2 concentration of its effluent brine in the range of two to three parts per million CO_2, and the O_2 concentration at an approximate 100-parts-per-billion level, if operated under

TABLE II-I

COST COMPARISON
PRESENT, REVISED, AND NORMALIZED PLANTS

Operating Temperature, °F	Capacity, gpd	Capital Cost, $	Operating Cost, $/1000 gal
230	1,000,000	1,604,406	1.20
275	1,433,000	1,624,285	0.95
300	1,812,000	1,678,627	0.83
300 Normalized	1,000,000	1,518,570	1.16

the conditions suggested in this report. "Alkalinity" values as reported from the presently precribed analytical procedures for the conversion plant, will not be a measure of the residual total CO_2 in the deaerator effluent. Reduction in the rate of stripping steam used (vapors from Effect XI) will result in an increase in the concentration of CO_2 and O_2 in the deaerator effluent. The present location of the deaerator in the plant flow system is considered proper.

8. The product water being pumped to Freeport is considerably more corrosive toward plain steel than is Freeport well water. The chlorinated, blended water, resulting from mixing the converted water with Freeport well water in the present proportion, is only slightly more corrosive to plain steel than chlorinated well water alone.

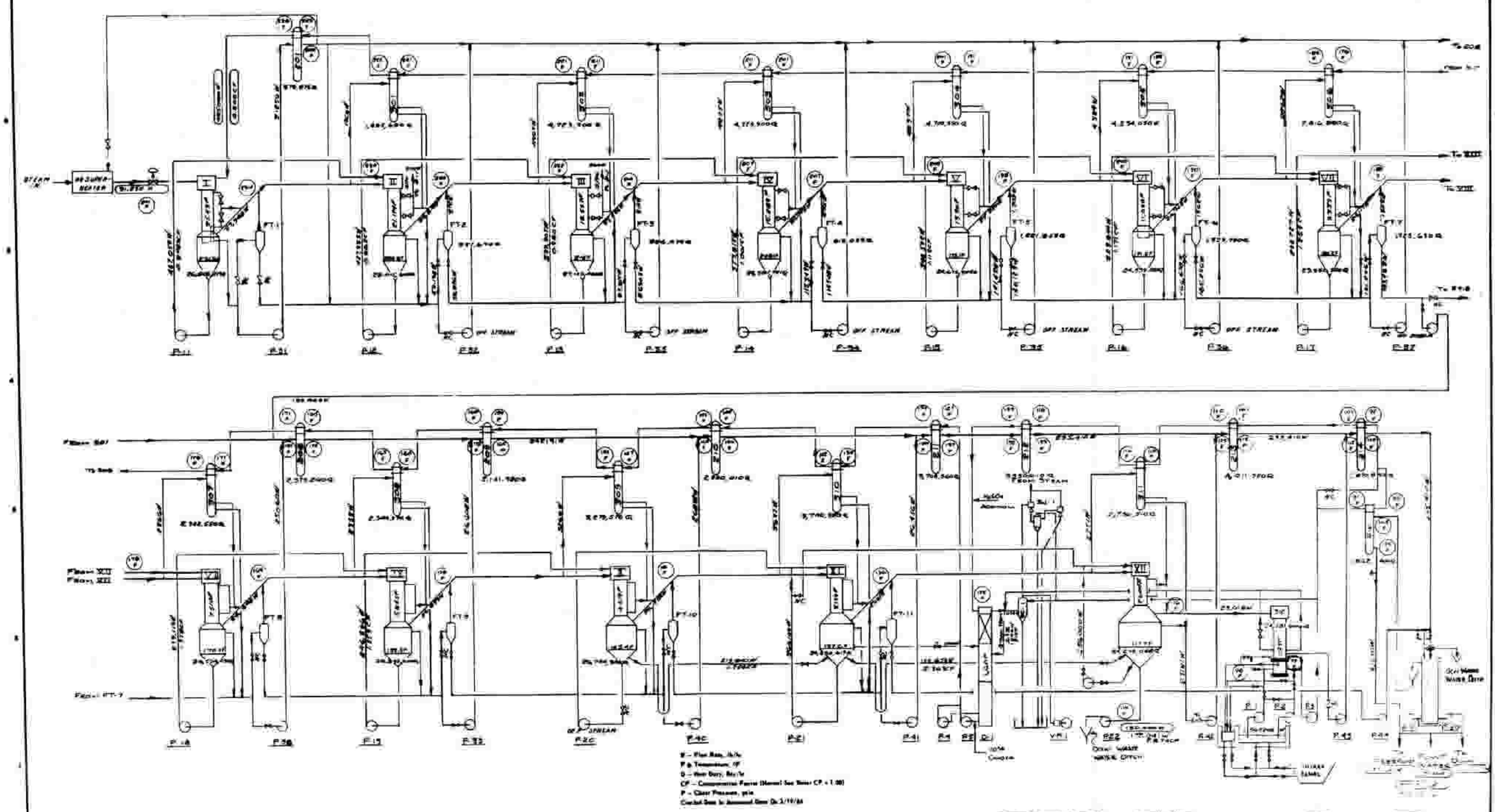
9. The corrosiveness of the product water is due to its lack of scaling properties, which correlates with its occasionally rather high CO_2 content. This condition can be economically corrected by any of several methods outlined in the body of this report.

Specific conclusions and recommendations concerning special problems studied in the evaluation will be found throughout this report.

SECTION III. HEAT AND MATERIAL BALANCE

A. Existing Plant Balance

Data used for this balance was taken August 19, 1963, and March 19, 1964. Temperatures were recorded to the nearest degree and flow rates were recorded to the nearest thousand pounds per hour. The steam fed to each evaporator steam chest was considered saturated at the recorded vapor-head temperature. Latent heat and pressure of the steam were taken from steam tables(23) (datum saturated liquid at $32^{o}F$). The properties of sea water and its concentrates were collected from the literature. The balance, Figure III-A-1, was calculated with the recorded sea-water flow rate of normal sea water, 3.51745 per cent total dissolved solids, as the feed to the process. The calculated production was two per cent above the recorded production for August 19, 1963 and five per cent below that recorded on March 19, 1964. The existing plant balance was used as the basis for the design calculations for the process equipment.



W – Flow Rate, lb/hr
T – Temperature, °F
Q – Heat Duty, Btu/hr
CP – Compensation Factor (Normal See Note: CP = 1.00)
P – Chest Pressure, psia
Control Data Is Assumed Data On 3/19/64

FILE NO. P-86-1

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ORIGINAL D/W NO.

DRAWN H. Gray DATE 2-27-64
DESIGNED DATE
TRACED DATE
CHECKED DATE
APPROVED DATE
APPROVED DATE

(7)

JOB NO. 7561

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT, TEXAS

SALINE WATER CONVERSION PLANT
PRESENT DEMONSTRATION PLANT NO. 1
HEAT AND MATERIAL BALANCE

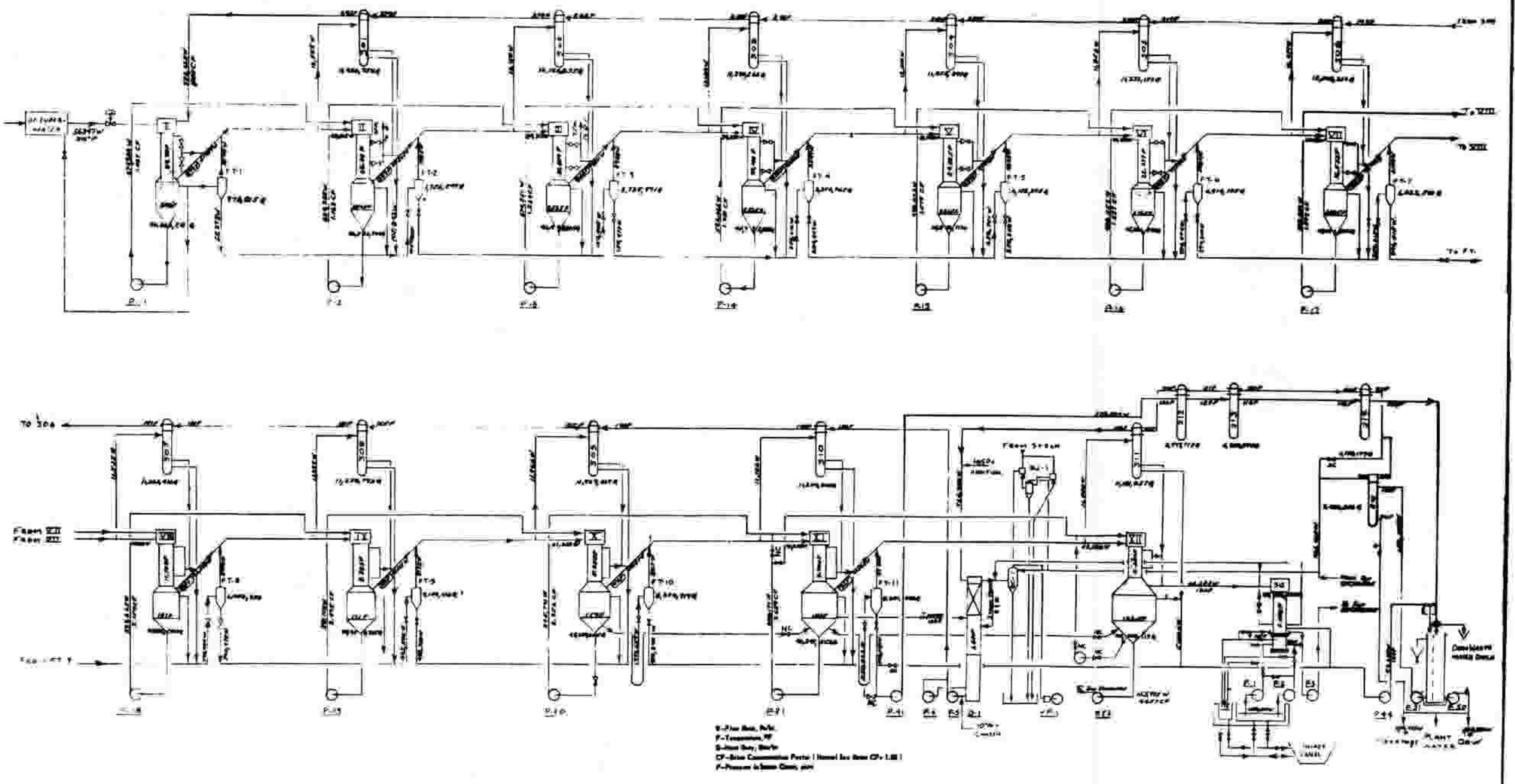
SCALE None
SHEET
Figure III-1

SECTION III. HEAT AND MATERIAL BALANCE

B. Revised Plant Balance

1. 300°F Revised Balance

The heat and material balance, Figure III-B-1, is based on a brine temperature of 300°F in Effect I and a brine concentration factor in Effect XII of five times normal sea water. The use of ion-exchange softening to remove 70 per cent of the calcium from the sea water feed allows operation within these limits without the formation of scale in Effects I or XII. The temperature of the vapor from Effect XII was set at 120°F by the temperature of available cooling water. The over-all temperature difference was divided to give an equal drop in temperature from one vapor head to the next. The steam requirement to Effect I, 56,347 pounds per hour at 316°F, was determined from an over-all heat-transfer coefficient based on representative operating data, the heat-transfer surface of Effect I and the temperature difference. The gross production for the plant operating at these conditions is 1,812,000 gallons per day with a steam economy of 11.1 pounds of water per pound of steam.



W–Flow Rate, lb/hr
T–Temperature, °F
Q–Heat Duty, Btu/hr
CF–Brine Concentration Factor (Normal Sea Water CF= 1.00)
P–Pressure in Steam Chest, psia

MARK	CO. ORD.	REVISION	BY	DATE	APP.	MARK	CO. ORD.	REVISION	BY	DATE	APP.	MARK	CO. ORD.	REVISION	BY	DATE	APP.

FILE NO. [illegible]

DRAWN [illegible] DATE [illegible]
TRACED E.E. HARRIS DATE 6-25-[illegible]
CHECKED [illegible] DATE [illegible]
APPROVED [illegible] DATE [illegible]

(9)

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS

SALINE WATER CONVERSION PLANT
PROPOSED HEAT AND MATERIAL BALANCES FOR
[illegible] OPERATION

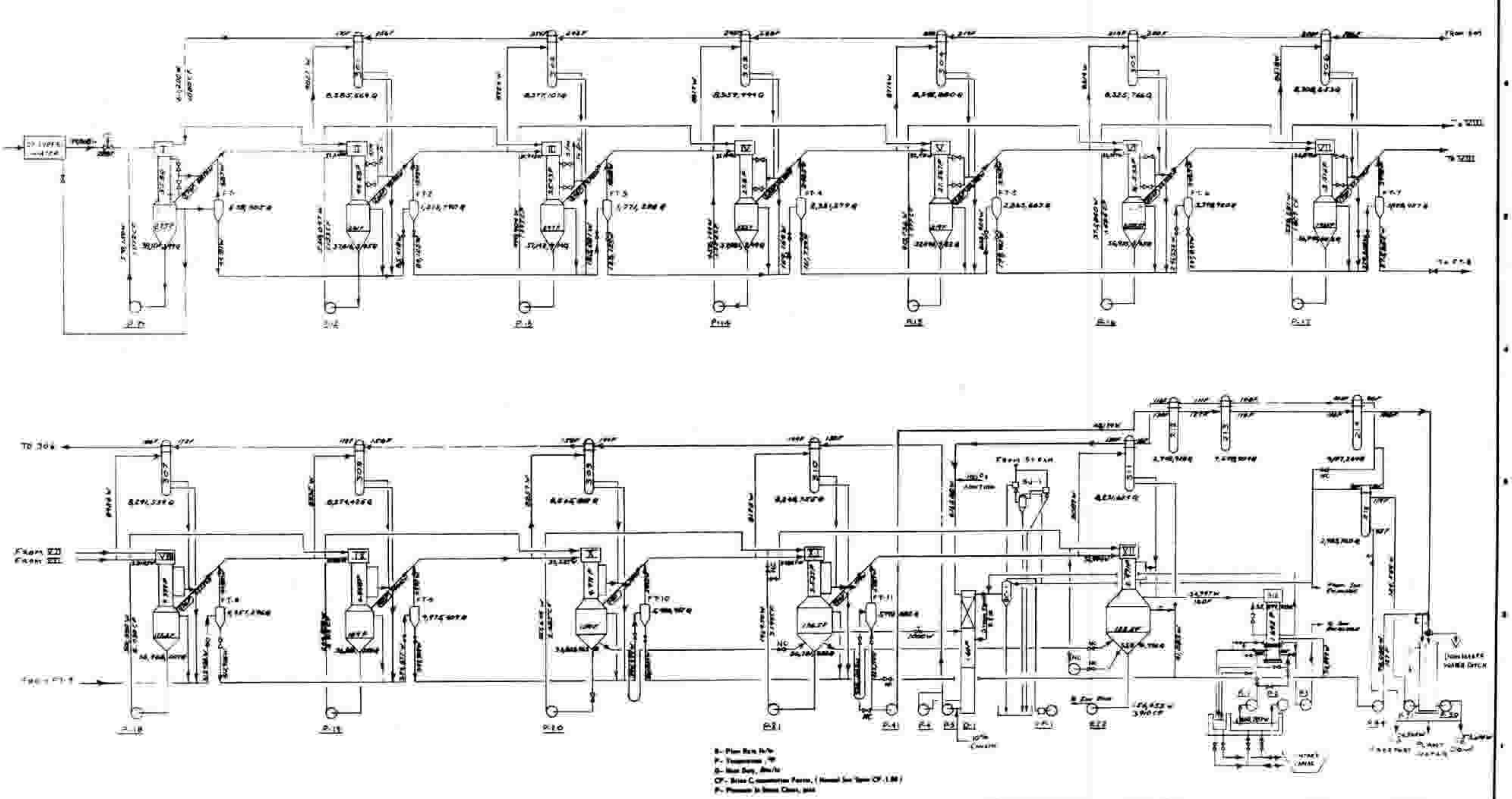
SCALE [illegible]
Figure III B-1

SECTION III. HEAT AND MATERIAL BALANCE

B. Revised Plant Balance

2. 275°F Revised Balance

The heat and material balance, Figure III-B-2, is based on a brine temperature of 275°F in Effect I and a brine concentration of four times normal sea water in Effect XII. The use of ion-exchange softening to remove 50 per cent of the calcium from the sea water feed allows operation within these limits without scale formation in Effects I or XII. The vapor-head temperature from Effect XII was set at 120°F. The over-all temperature difference was divided to give an equal difference between vapor-head temperatures. The steam requirement to Effect I, 44,868 pounds per hour at 288°F, was determined in the same manner as for the 300°F balance. The gross production for the plant operating under these conditions is 1,433,000 gallons per day with a steam economy of 11.1 pounds of water per pound of steam.



W- Flow Rate lb/hr
T- Temperature, °F
Q- Heat Duty, Btu/hr
CF- Brine Concentration Factor, (Normal Sea Water CF 1.00)
P- Pressure in Steam Chest, psia

FILE NO. F-III-1

MARK	CO-ORD	REVISION	BY	DATE	APP.

DRAWN T. LEARY
CHECKED C.M. LEE
TRACED E.E. HARRIS
CHECKED
APPROVED
APPROVED

(11)

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT, TEXAS

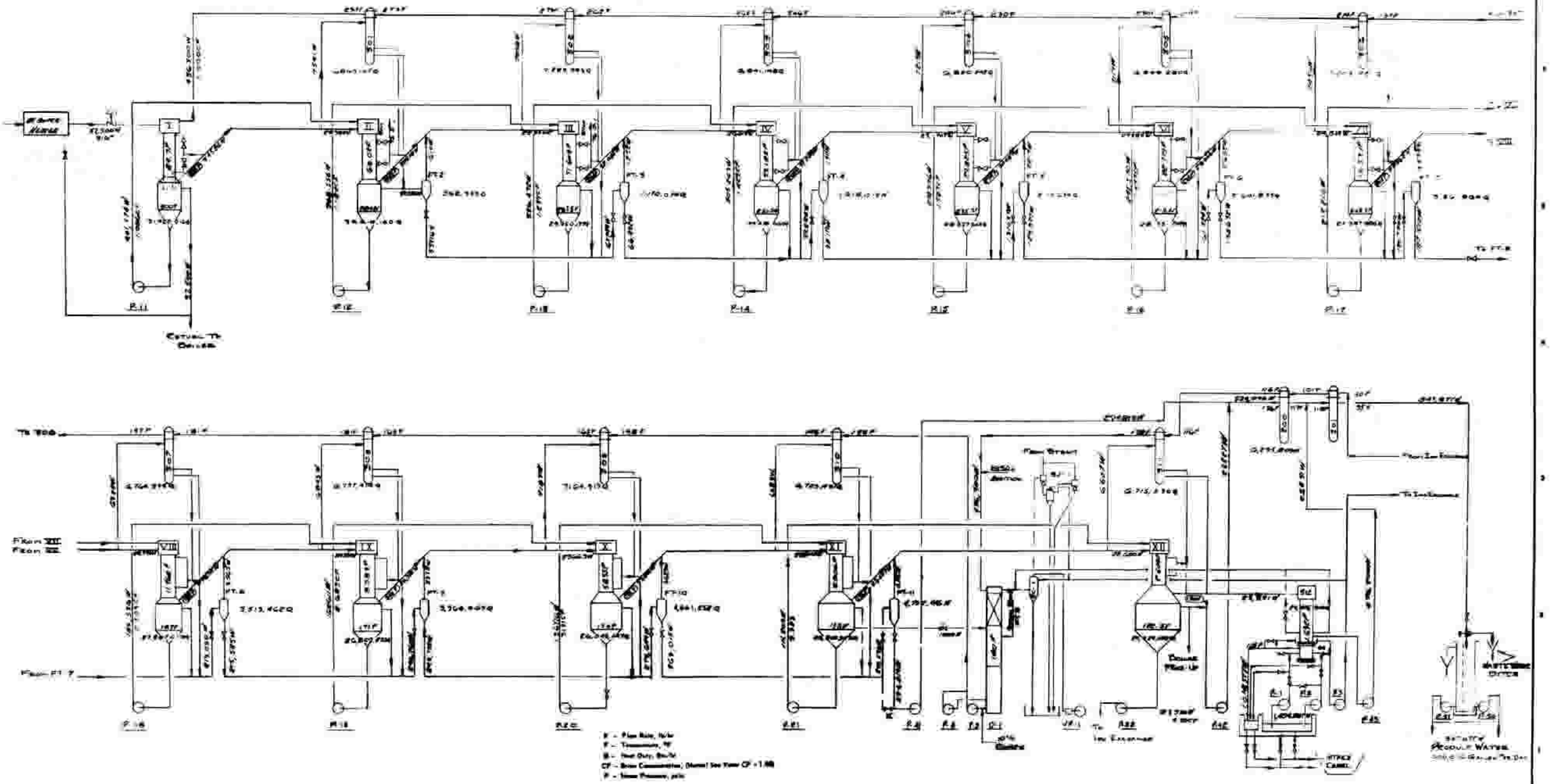
PROPOSED HEAT AND MATERIAL BALANCES FOR 275 °F OPERATION

SCALE None
Figure III-1

SECTION III. HEAT AND MATERIAL BALANCE

C. Normalized Plant Balance

The normalized balance, Figure III-C-1, is based on the 300°F revised balance. The process conditions are the same, with the sea water feed rate and steam rate to Effect I reduced by the ratio of the production of the normalized plant to the production of the revised 300°F plant. The condensate from steam fed to Effect I is returned to the boiler and not carried through the system; therefore, flash tank number one is not required in the normalized plant.



F – Flow Rate, lb/hr
T – Temperature, °F
Q – Heat Duty, Btu/hr
CF – Brine Concentration, (Normal Sea Water CF = 1.00)
P – Steam Pressure, psia

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ORIGINAL B/E NO.

JOB NO. 7301

DRAWN J.L. Gray DATE

DESIGNED G.M. Lowe DATE 7-6-64

TRACED J.V. Fay DATE 7-7-64

CHECKED G.M. Lowe DATE 7-7-64

APPROVED D.L. Brown DATE 7-8-64

APPROVED DATE

SEAL

(13)

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS

SALINE WATER CONVERSION PLANT
NORMALIZED PLANT HEAT & MATERIAL
BALANCE FLOWSHEET

SCALE None

SHEET

Figure III C-1

SECTION IV. GENERAL PLANT DESIGN

A. Intake Design

1. Description

Inlet capacity is provided by two 30-inch diameter steel lines that originate in the Ethyl-Dow sea-level intake canal. The lines are pile-supported in the canal and they extend underground 380 feet to the intake structure.

The intake structure is a reinforced concrete pit that contains a traveling screen, two pumps, and a recycle chamber. It is approximately 50 feet long by 15 feet wide by 12 feet deep.

SECTION IV. GENERAL PLANT DESIGN

A. Intake Design

2. Technical Evaluation

Basically, the intake structure is well designed and is adequate for the intended service. Nothing was found that indicates any modification to the existing facility is needed.

Silt in the incoming water is possibly a problem, and consideration has been given to pretreating the water. Effective desilting of sea water can be achieved by treating with magnesium hydroxide in a settling pond. The estimated cost of an installation is $50,000. The increased operating and maintenance costs, caused by silt, are not well defined, but they are not considered to be sufficient to justify a $50,000 expenditure.

Screening is provided by a traveling screen equipped with 1/2-inch screen fabric. The screen is operated manually, and the frequency of washing is determined by observing the drop across the screen. More favorable results could be obtained if a smaller mesh screen were used. The velocity across the screens is less than 0.5 feet per second; therefore, head loss should not be a problem with the finer mesh.

A few physical features were noted that should not be repeated in future installations, and they are submitted for future reference.

a. Untreated timber piles were used to support the intake lines. These piling are exposed to sea water and are vulnerable to attack by marine borers.

b. Steel pipe was used for the gravity intake lines. Concrete culvert pipe will give satisfactory service and can be installed more economically.

c. The elaborate configuration used for the bottom of the intake pit adds to the cost and does not contribute to the performance of the installation.

SECTION IV. GENERAL PLANT DESIGN

A. Intake Design

3. Recommendations

a. The screen fabric on the traveling screen should be replaced with smaller mesh as normal replacement is required. The existing screen is 1/2-inch and six-mesh screen is recommended.

b. Additional experimental work should be done to determine if silt can be effectively removed in the existing 30-foot diameter tank.

B. Preheater and Cross-Exchanger Design

1. Present Plant Exchanger Design

The comparison of observed and calculated values of over-all heat-transfer coefficient, based on the correlation recommended by Kern(24) was made. Preheaters 301, 302, 303, and 306, and cross exchanger 208 were found to have operating values above the calculated over-all coefficients. The values of the operating and calculated coefficient, Table IV-B-1-I, show a decreasing trend from the high temperature condition in preheater 301 to the low temperature conditions in preheater 311. The decreasing trend is also shown in exchangers 208, 209, 210, 211, 212, 213, 214, and 215, although it is not as pronounced as in the preheaters. The treatment of the preheaters was based on the correlation for a vertical condenser with corrections for the effect of vapor velocity on the shell-side film coefficients. The fouling resistance was found to be high at the low-temperature end of system for both the 200-series and 300-series exchangers. There was a drop in fouling resistance between exchanger 212, immediately preceding the deaerator, and exchanger 211, immediately following the deaerator. It was found that the addition of baffles on the shell side of the 200-series increased the over-all coefficient from 27 per cent to 52 per cent of present calculated values. The increase in over-all coefficient was attributed to the increase in liquid velocity and turbulence created by the changes in direction of flow. Baffles were found to have no significant effect on the 300-series condensers.

The installation of baffles in the 200-series exchangers cannot be justified since most of these exchangers should be replaced with flash tanks. Section IV-B-2 shows that the flash tanks are capable of handling the heat recovery from the product water as well as the 200-series exchangers.

TABLE IV-B-1-I

HEAT-TRANSFER COEFFICIENTS AND FOULING RESISTANCES FOR PRESENT PLANT HEAT EXCHANGERS

Exchanger	Over-all Coefficient: Operating, Btu/sq ft-hr-°F	Over-all Coefficient: Calculated, Btu/sq ft-hr-°F	Fouling Resistance, °F-hr-sq ft/Btu
301	848.6	659	-0.00034
302	831.9	711	-0.00020
303	733.9	731	-0.000005
304	518.9	668	0.00043
305	341.7	669	0.00143
306	928.7	594	-0.00061
307	362.8	653	0.00123
308	542.1	577	0.00011
309	389.5	529	0.00068
310	316.2	522	0.00125
311	55.2	526	0.01620
201	121.1	195	0.00306
208	380.2	351	-0.00022
209	213.7	344	0.00177
210	87.4	359	0.00865
211	212.9	276	0.00106
212	95.6	288	0.00693
213	75.7	279	0.00963
214	106.3	252	0.00543
215	51.5	169	0.01349

B. Preheater and Cross-Exchanger Design

2. Heat Recovery

A comparison of methods of heat recovery from the product-water stream was made by means of heat and material balances. The two cases studied were the present operation and the present operation with exchangers 201, 208, 209, 210, and 211 replaced by flash tanks. The latter case eliminates 6,743 square feet of heat-transfer surface from the system while there is no significant change in production or steam economy as shown in Table IV-B-2-I. All equipment other than that mentioned above was the same for both cases in the comparison.

TABLE IV-B-2-I

COMPARISON OF HEAT RECOVERY FROM PRODUCT WATER BY FLASH EVAPORATION AND/OR LIQUID-LIQUID CROSS EXCHANGE

	Present Operation	Estimated Operation
Equipment	HE-201, FT-2 thru 7 HE-208 thru 215	FT-1 thru 11 HE-212 thru 215
Production, lbs/hr	342,209	342,470
gal/day	984,167	984,918
Steam Economy lbs water/lb steam	10.95	10.96

B. Preheater and Cross-Exchanger Design

3. Revised Plant Exchanger Design

The preheater and cross-exchanger heat-transfer area requirements were calculated on the bases of the heat load and temperature difference predicted by the revised heat and material balances. The overall heat-transfer coefficients used in the design for the revised cases were calculated from present operating data and are tabulated in Table IV-B-3-I. Exchangers 201, 208, 209, 210, and 211 were not considered in the revised cases and therefore were not designed for these requirements. These vessels were replaced by flash tanks to recover heat from the product water.

The present heat exchangers with the exception of exchangers 309 and 311 were found to be adequately sized to handle the load required by the 275°F revised plant balance. Exchanger 309 requires the addition of 44 tubes, and exchanger 311 requires 36 additional tubes. Each of these exchangers has the space needed for the additional tubes.

The heat load required by the 300°F revised plant balance necessitates that exchangers 301, 302, 303, 304, 305, 306, 307, 212, 213, 214, and 215 be tubed out. The exchangers 308, 309, 310, 311, and 312 must be replaced to meet the required heat load. Exchanger 308 was redesigned to have a shell 29 inches in diameter with 376 tubes. Exchangers 309, 310, and 311 were redesigned as 31-inch shells with 454 tubes. The final condenser, 312, was redesigned with 1000 tubes 20 feet long in a 48-inch shell.

The exchangers for the revised plant cases are the same as for the present plant with changes mentioned above. The flow pattern for the revised plant is the same as present flow with one exception, the sea water feed passes through the 212 exchanger before it enters 311 preheater.

TABLE IV-B-3-I

HEAT-TRANSFER AREA COMPARISON OF PRESENT OPERATION AND REVISED OPERATIONS FOR HEAT EXCHANGERS

	Area, sq ft[1]			
Exchanger	Present	Tubed Out	Required for, 275°F	300°F
301	1796	1796	1361	1744
302	1388	1796	1260	1672
303	1435	1796	1223	1565
304	1571	1796	1336	1709
305	1796	1796	1331	1702
306	1707	1796	1494	1796
307	1644	1796	1355	1733
308	1796	1796	1533	1959
309	1445	1796	1672	2213
310	1738	1796	1689	2156
311	1608	1796	1796	2124
312	4189	4189	3092	5077
201	533	963	Not required	
208	1173	2409	Not required	
209	1524	2409	Not required	
210	1628	2409	Not required	
211	1885	2409	Not required	
212	1858	2409	681	632
213	2147	2409	1381	1575
214	2304	2409	1727	1178
215	3037	3037	2323	2280

[1] Based on one-inch OD, 18-BWG tubes

B. Preheater and Cross-Exchanger Design

4. Normalized Plant Exchanger Design

The exchangers for the normalized plant were sized from the exchangers required for the revised plant for 300°F operation. The heat-transfer areas were reduced, by the ratio of normalized sea-water feed rate to the sea-water feed rate for the revised plant, from the area required for 300°F revised operation. Table IV-B-4-I gives the tabulation of the normalized heat-exchanger designs. Exchangers 212, 213, 214, and 215 were replaced by two exchangers 200 and 201, to handle the cross-exchanger load. The exchangers were calculated for a required area and tube count with the shell of the nearest standard diameter large enough. The vessels were designed with the shell completely tubed out.

TABLE IV-B-4-I

HEAT-EXCHANGER DESIGN FOR NORMALIZED PLANT

Exchanger	Required Area, sq ft	Required Tube Count	Shell Diameter, in.	Design Tube Count
301	1057	202	23-1/4	232
302	1013	194	23-1/4	232
303	948	181	23-1/4	232
304	1036	198	23-1/4	232
305	1031	197	23-1/4	232
306	1200	229	23-1/4	232
307	1050	201	23-1/4	232
308	1187	227	23-1/4	232
309	1341	256	25	282
310	1307	250	25	282
311	1287	246	25	282
312	3077	588	35	592
200	1454	278	25	282
201	2109	403	31	454

C. Deaeration Design

1. Determine the minimum performance characteristics for a satisfactory deaeration system, relocate, and redesign the present deaerator, if necessary.

a. Conclusions and Recommendations

(1) The present deaerator is adequate in size, and in general, its design is proper to reduce both the O_2 content and CO_2 content of the incoming brine to satisfactory levels.

(2) The existing location of the deaerator as shown in Figure III-A-1 is considered to be the proper location.

(3) The present (May, 1964) packing, consisting of a 16-foot depth of three-inch ceramic Raschig rings should be replaced with an eight-foot depth of 3-3/4-inch size polystyrene "Maspac FN-90" packing to effect an improvement in deaerator performance with respect to decarbonation.

(4) Packing requirements for three proposed sets of conditions have been calculated and are listed in Table IV-C-I. In each case, "Maspac FN-90" is the type of packing recommended.

(5) A savings in capital cost for the deaerator of between \$1000 and \$2000 can be effected in the normalized plant by constructing the deaerator shell 10 feet shorter than the existing unit.

(6) In each of the cases listed in Table IV-C-I, the amount of packing recommended is probably a very conservative (i.e., "safe") value. The packing requirement given is based on literature values for stripping O_2 and CO_2 from water using air. Stripping with steam will introduce more favorable conditions for the apparent transfer surface required, which cannot be quantitatively evaluated from existing data. (see Discussion under paragraph IV-C-1-c.)

TABLE IV-C-I

CALCULATED PACKING REQUIREMENTS FOR EXISTING DEAERATOR

Case	Conditions	Brine Flow, gpm	Packed Height, ft	Volume of Packing, cu ft
0	Existing	490,000	8	225
I	275°F Revised Plant Operation	611,200	10	282
II	300°F Revised Plant Operation	726,420	11	310
III	300°F Normalized Plant	436,400	7	198

NOTE: The above packing requirements are based on an entering brine containing 105 ppm total CO_2 and 9.5 ppm O_2; and a leaving brine containing 0.5 ppm CO_2 and 0.01 ppm O_2, and assumes the packing is 3-3/4-inch Maspac FN-90.

(7) Based on Freeport Conversion Plant operating records, the deaerator is able to reduce O_2 to below detectable values with no packing. The CO_2 stripping effectiveness under these conditions is not known with certainty at this time.

(8) The present deaerator, or any other deaerator of similar type, will never utilize its packing and stripping steam effectively. This situation is inherent in the requirements imposed on it (see Discussion under paragraph IV-C-1-c). This does not reflect poor choice of deaerator type or poor design of existing type to do the existing job.

(9) Recommendations concerning operation of the deaerator appear in Sections V-A-2 and V-A-3 of this report.

b. Description of Work Done

Basic data were obtained from literature surveys to permit calculation of the values and relationships plotted on Figures IV-C-1 through IV-C-7, and shown in Tables IV-C-I through IV-C-VI. These curves were then used in subsequent computations involving equilibria in the CO_2 - sea water system or O_2 - sea water relationships.

No applicable data could be found in the literature for the stripping of either O_2 or CO_2 from fresh water or from sea water by using steam. Adequate design data does exist for desorbing both CO_2 and O_2 from fresh water by stripping with air. Some of these are listed in Tables IV-C-II and IV-C-III. Since the liquid film is the controlling resistance to mass transfer in the desorption of O_2 and CO_2 from fresh water, and since the viscosity of sea water approximates that of fresh water, these data were assumed to be valid for steam.

In all of the calculations, it was assumed that the upward flow of stripping steam in the deaerator was equal to the flow of leaving vapors. Although this is not strictly true, this assumption permits the use of workable methods and yields satisfactory results without employing other assumptions further removed from known conditions.

TABLE IV-C-II

DESORPTION OF CO_2 AND O_2 FROM WATER BY AIR, USING 1/2-INCH TO 2-INCH SIZE RASCHIG RINGS

Solute Gas	Temp., °C	L, $\frac{\text{lbs } H_2O}{\text{hr-sq ft}}$	G, $\frac{\text{lbs } H_2O}{\text{hr-sq ft}}$	K_La, $\frac{\text{lb mols/hr/cu ft}}{\text{lb mols/cu ft}}$	HTU, ft	Investigator and Lit. Ref.
O_2	23	20,000	230	-	1.8	Sherwood and Holloway(44)
O_2	21.5	12,200	230	130	1.5	Sherwood and Holloway(44)
O_2	21.5	32,000	230	155	3.3	Sherwood and Holloway(44)
CO_2 - O_2	22.5	4,000	100	-	1.5	Deed, et al(13)
CO_2	21	15,000	various	100	-	Koch, et al(25)
CO_2	15	10,000	various	75	-	Allen, H. V.(1)
CO_2	8.3	10,000	various	80	4	Shulman and De Gouff(47)

TABLE IV-C-III

EFFECT OF TEMPERATURE ON K_La AND HTU FOR O_2 AND CO_2 BETWEEN AIR AND WATER

From Sherwood and Holloway(44)

Temp., °C	K_La, $\frac{\text{lb mols/hr/cu ft}}{\text{lb mols/cu ft}}$	HTU, ft
10	44	0.7
20	55	0.6
30	70	0.45
40	85	0.38
50	110[1]	0.30
110	320[1]	0.12

[1] Extrapolated

FIG. IV.-C-1

SOLUBILITY LIMIT OF OXYGEN IN SEAWATER IN EQUILIBRIUM WITH NORMAL AIR

FROM FOX, PRESENTED BY HARVEY (22)

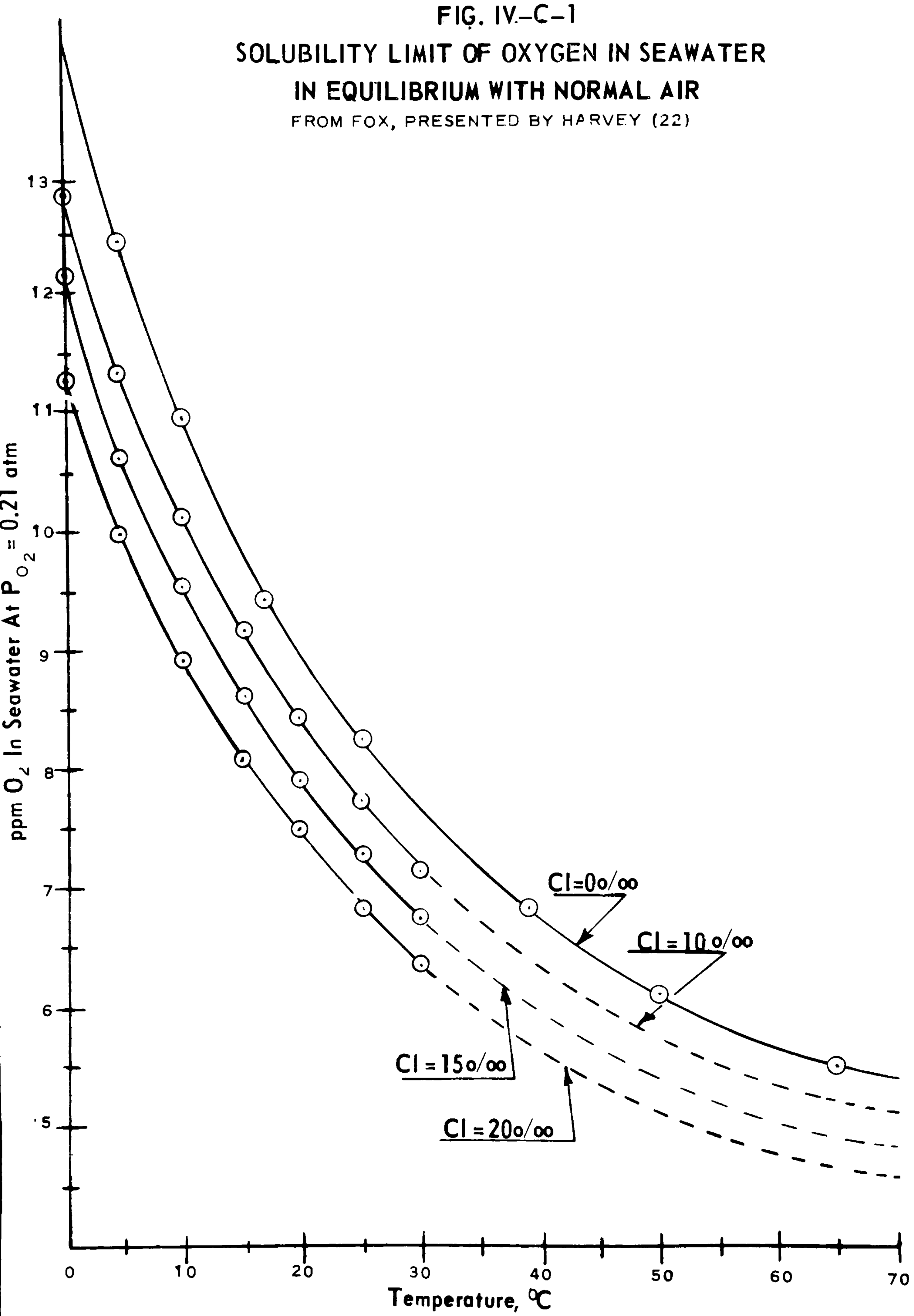


FIG. IV-C-2

SOLUBILITY OF CO_2 IN SEAWATER

FROM BOHR'S DATA, PRESENTED BY HARVEY (21)

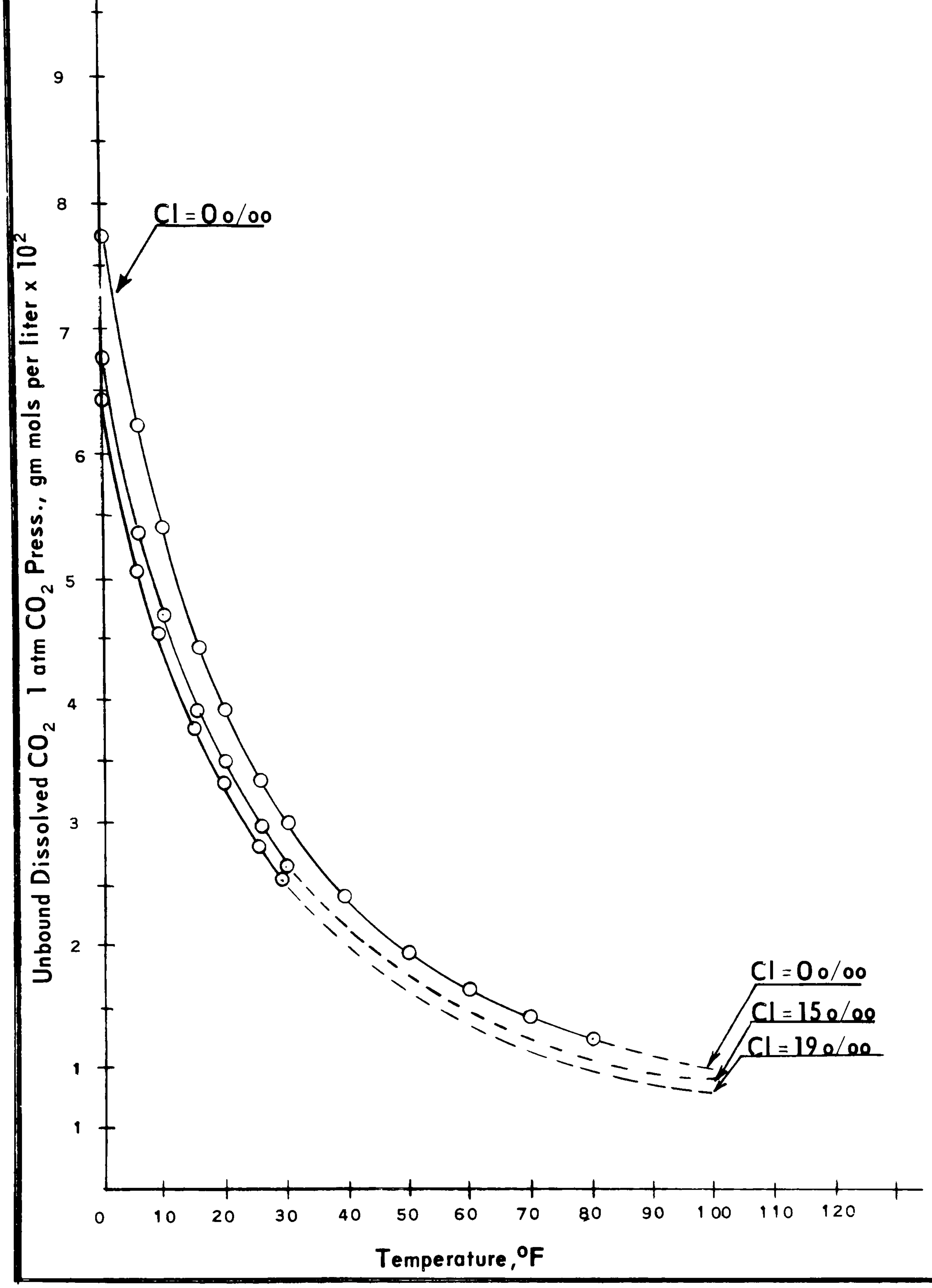


FIG. IV-C-3

DISSOCIATION OF CO_2 IN SEAWATER

$$K_1' = \frac{[HCO_3^-][H^+]}{[CO_2]}$$

DATA:

0o/oo CL. HAMER, ET AL. (16)

15o/oo CL: FROM BUCH, PRESENTED BY HARVEY (20)

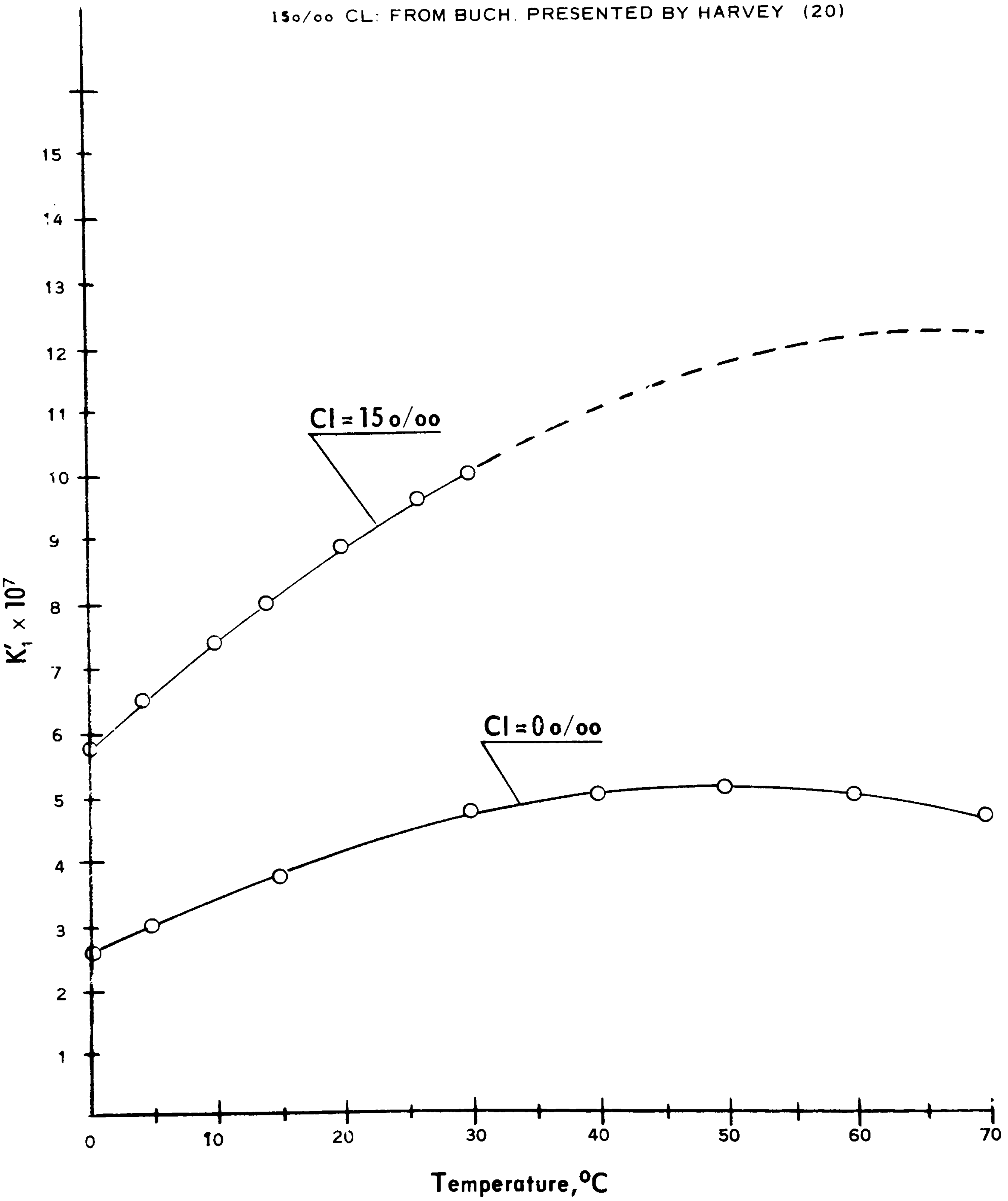


FIG. IV-C-4

DISSOCIATION OF CO_2 IN SEAWATER

$$K'_2 = \frac{[CO_3^{=}][H^+]}{[HCO_3^-]}$$

0 o/oo CL: HAMER, ET AL (16)

15 o/oo CL: FROM BUCH. PRESENTED BY HARVEY (20)

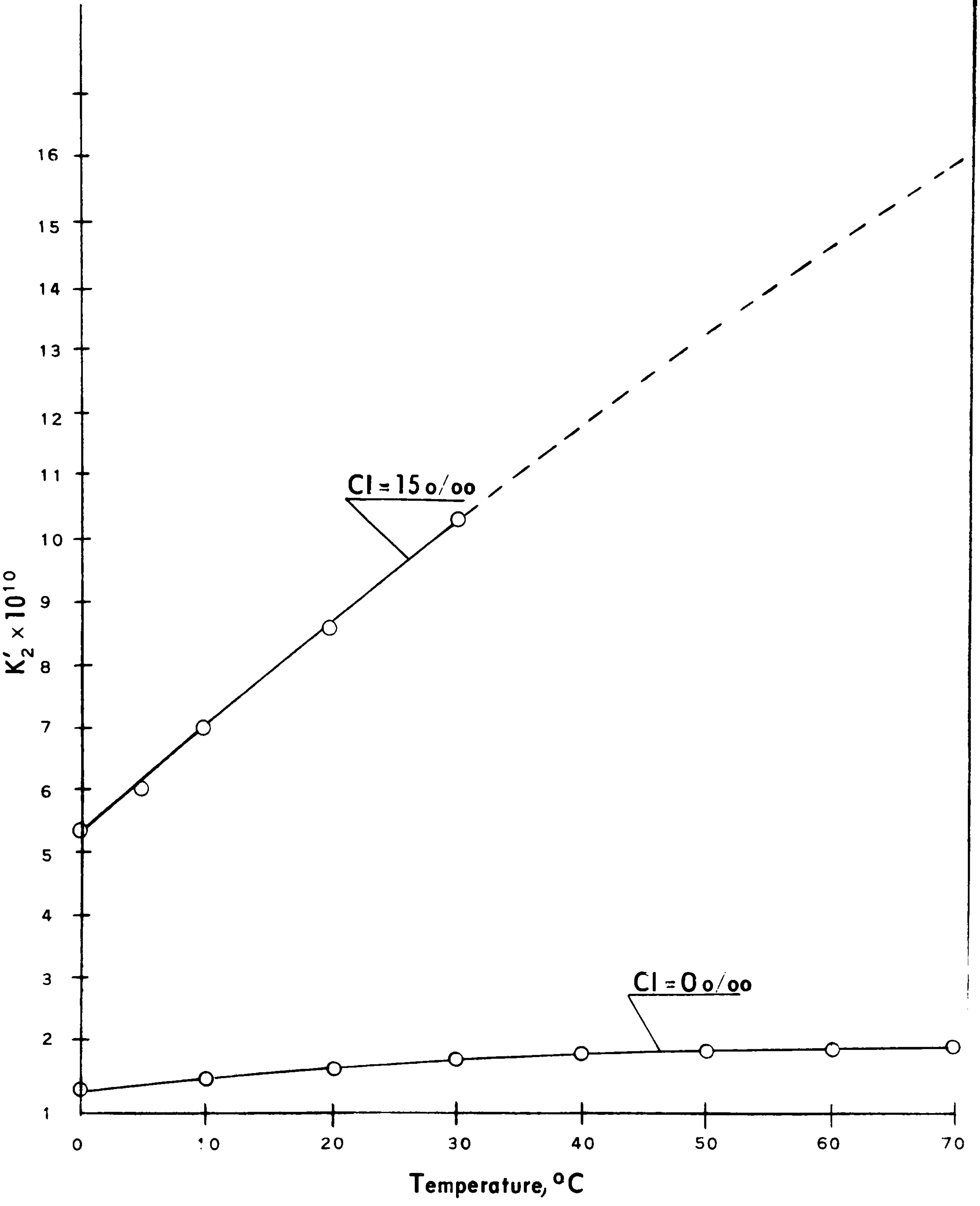
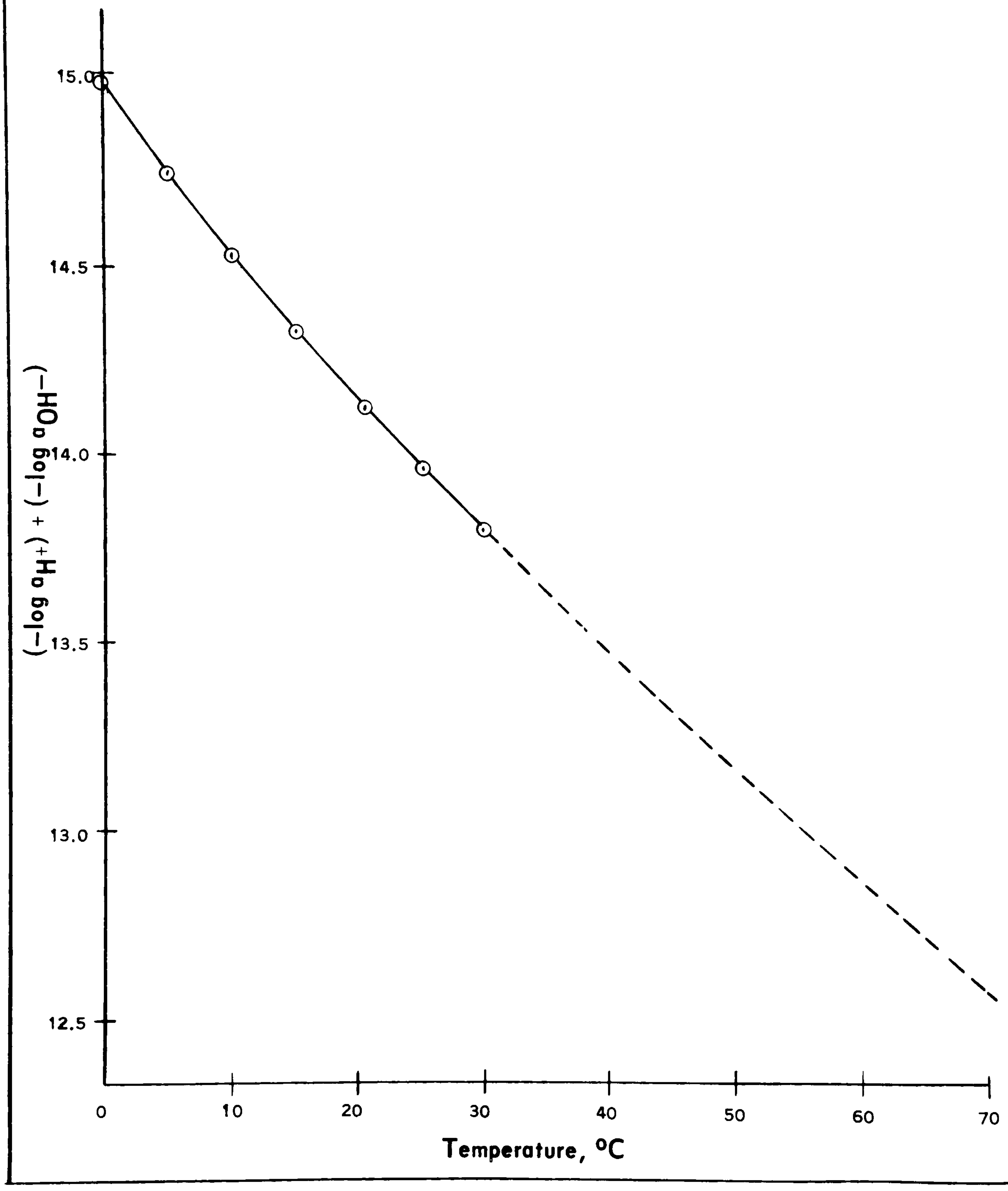


FIG. IV-C-5
DISSOCIATION OF H_2O IN SEAWATER

CHLORINITY = 19o/oo

FROM COOPER, PRESENTED BY HARVEY (18)



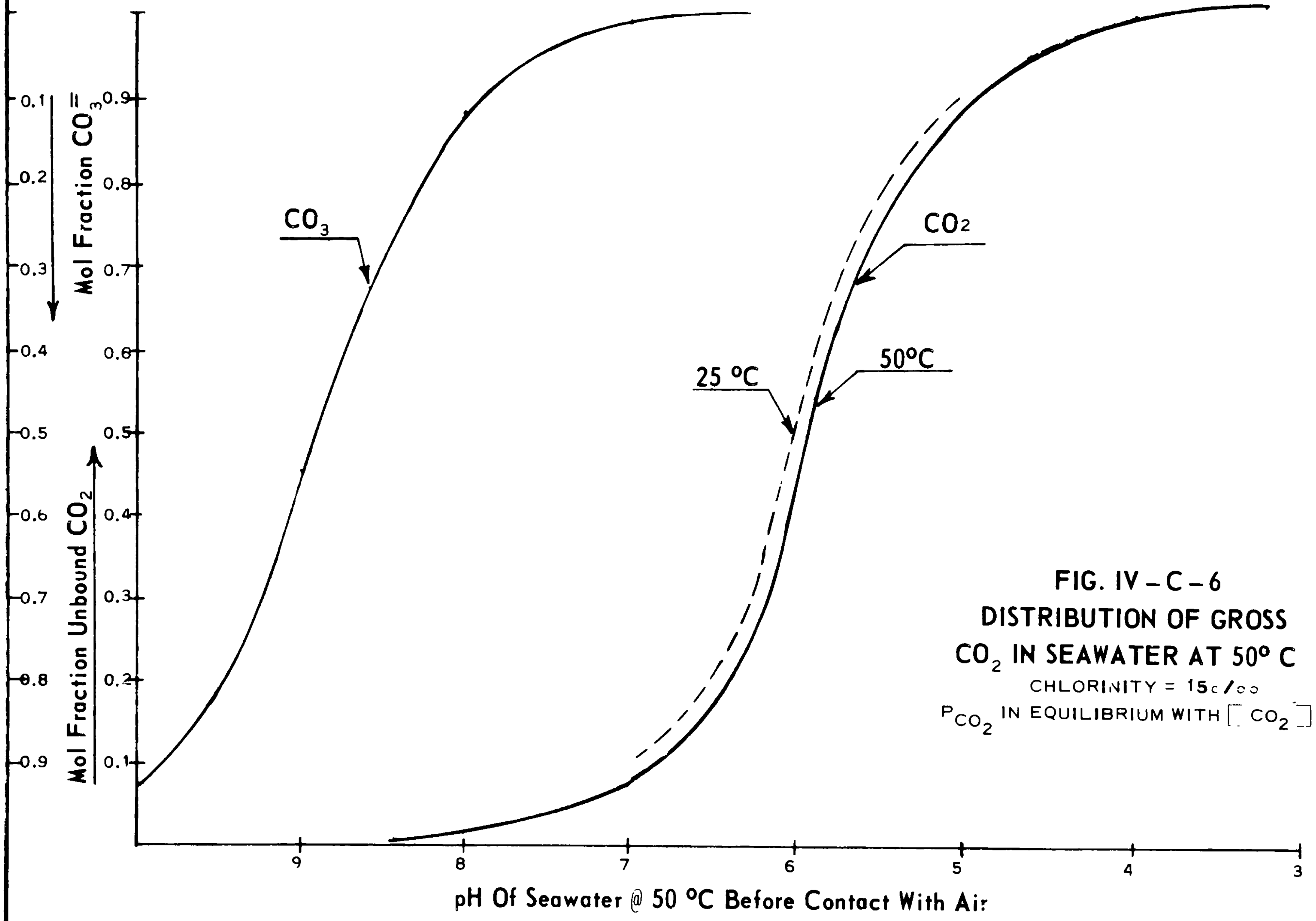


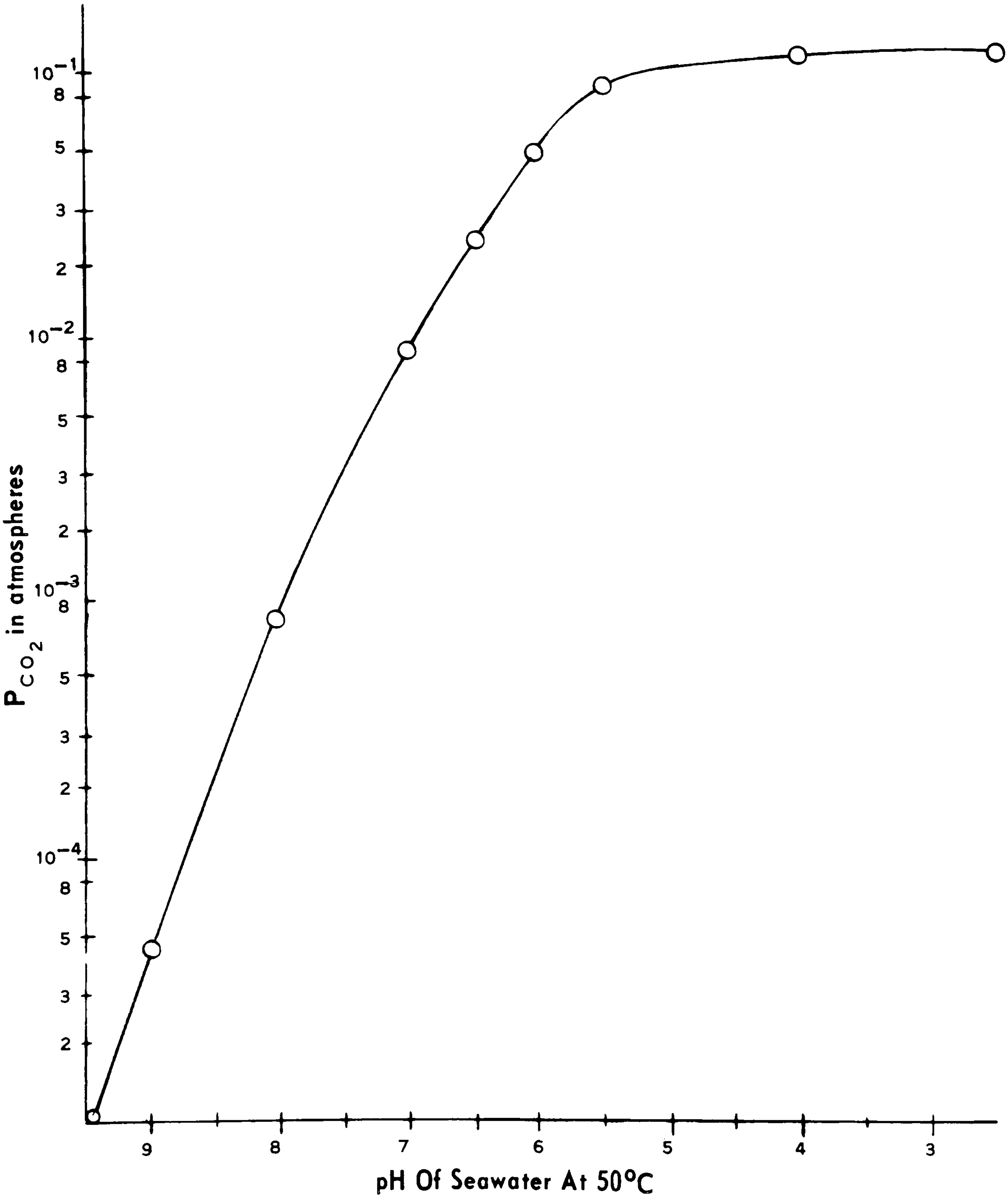
FIG. IV – C – 6
DISTRIBUTION OF GROSS
CO_2 IN SEAWATER AT 50° C
CHLORINITY = 15 °/oo
P_{CO_2} IN EQUILIBRIUM WITH [CO_2]

FIG. IV-C-7

EQUILIBRIUM PRESSURE OF CO_2 OVER SEAWATER

T=50°C (122 °F) ; CHLORINITY = 15‰

GROSS CO_2 CONTENT = 2.09×10^{-3} MOLS CO_2 / LITER



Carbon dioxide and O_2 balances were made over the deaerator on April 10, 1964. Duplicate sets of samples were taken of the sea water fed to the deaerator and of the effluent sea water during a test period in which the pH of the influent sea water was maintained at a maximum value of four pH units. The dissolved O_2 was determined immediately on one set of duplicate samples by a modified Winkler method. The total CO_2 was determined on another set of duplicate samples gravimetrically in an Ascarite train. The analytical results were then used to compute the operating conditions of the deaerator, shown on Figures IV-C-8 and IV-C-9, using the well-known method described by Sherwood and Pigford(45). Calculations of the packing requirement for the three sets of revised conditions shown in Table IV-C-I also employed the method described by Sherwood and Pigford(45).

On the day the deaerator test run was made, the chlorinity of the inlet brine was approximately 15 parts per thousand, and the total CO_2 content was 92 parts per million. Since the yearly average chlorinity and gross CO_2 content of sea water at Freeport approximate these two values, respectively, they have been used as bases for computing the working curves mentioned above. (Actually, 90 parts per million $CO_2 = 2.09 \times 10^{-3}$ molar has been used for the bases of CO_2 calculations.)

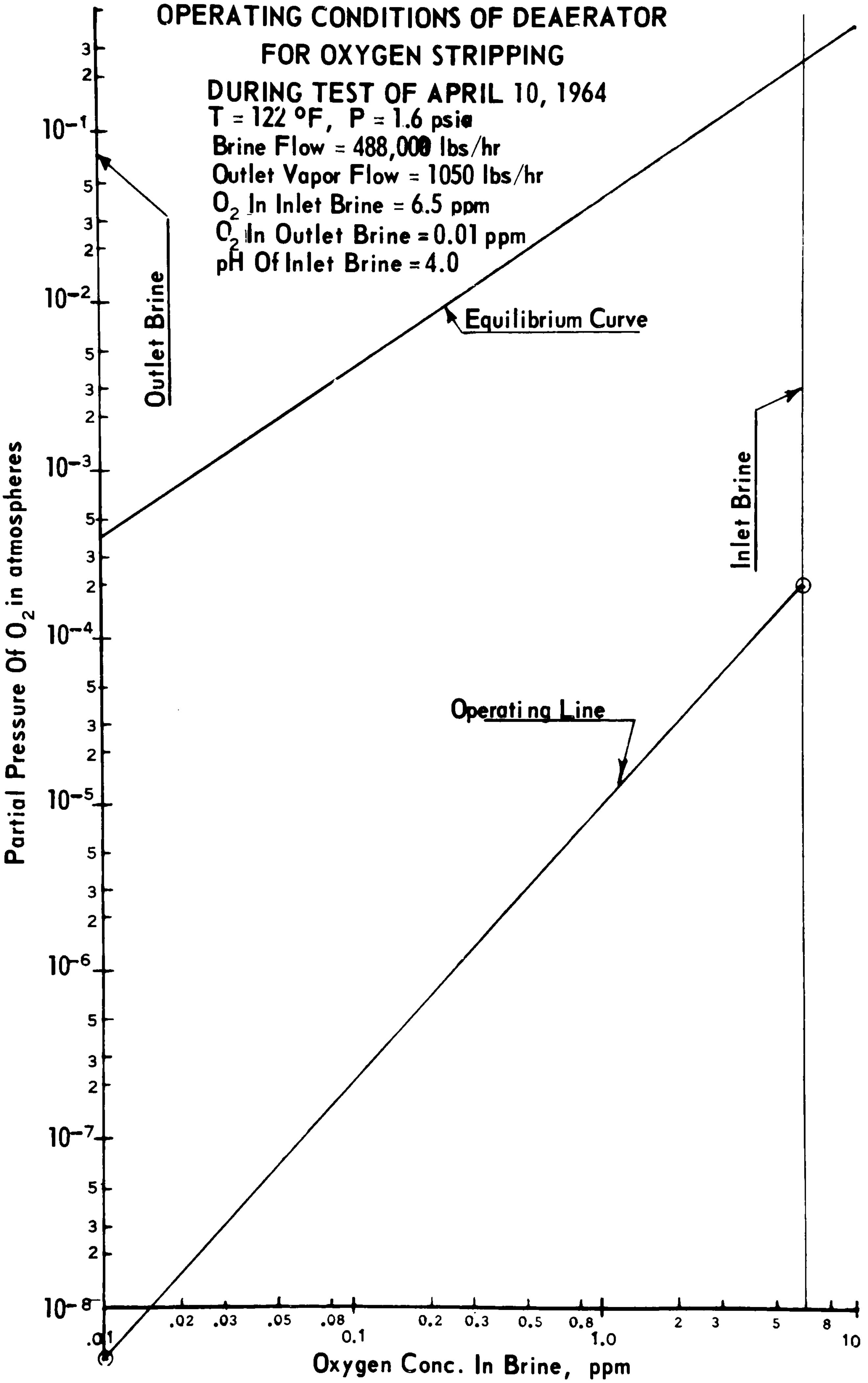
c. Discussion

Deaerators in service in steam-power generation service are claimed to attain residual dissolved O_2 concentrations of leaving water of between 0.007 parts per million and 0.35 parts per million(8) depending on the type. A satisfactory level of dissolved O_2 would be considered to be 0.005 parts per million for low or medium pressure service up to 400 pounds per square inch, gauge (457°F saturated steam temperature).

For the Freeport Conversion Plant, in consideration of the lower operating temperatures, a dissolved O_2 concentration of 0.010 parts per million should be satisfactory. The opportunity for leakage of

FIG.. IV-C-8

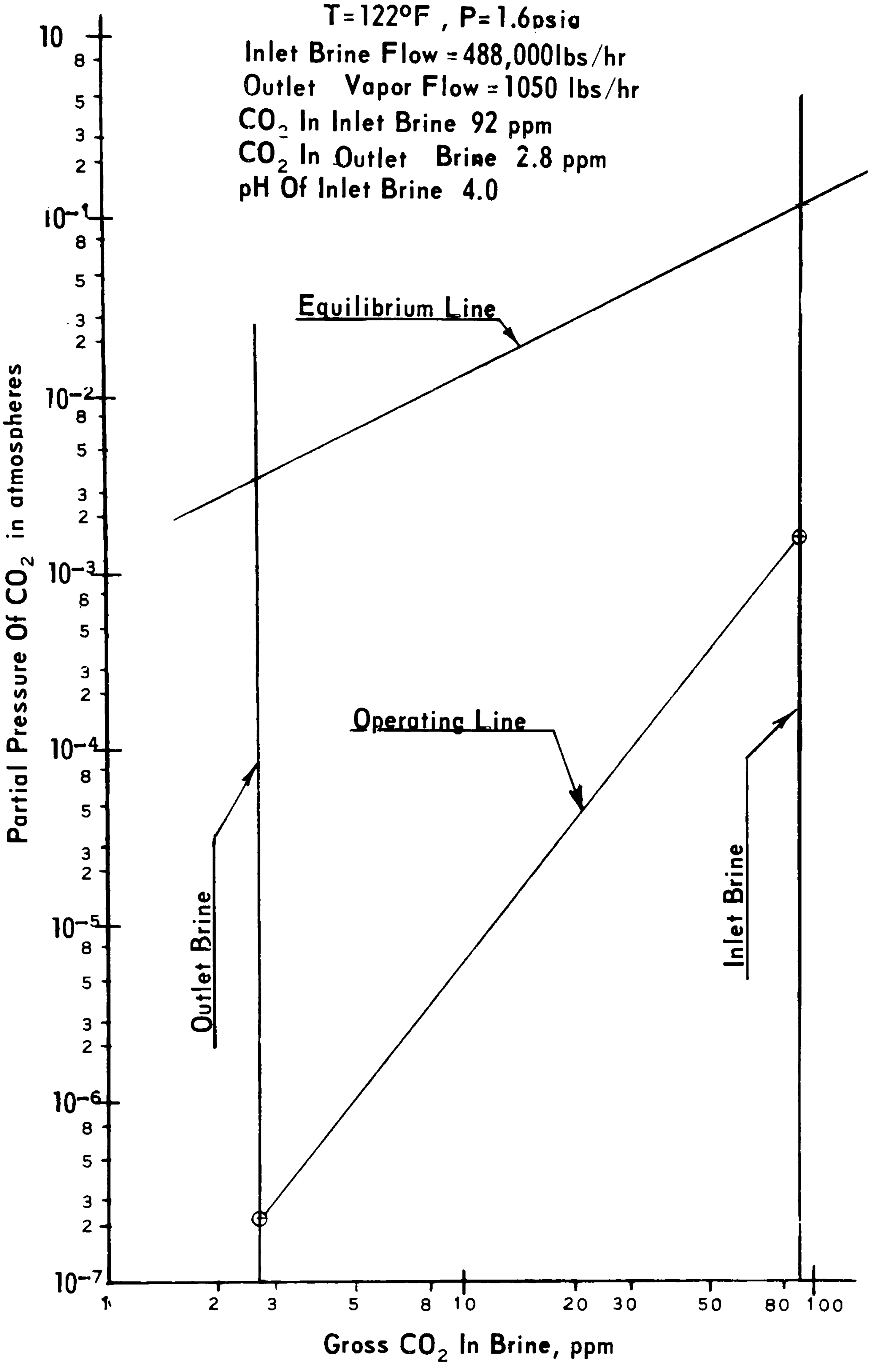
OPERATING CONDITIONS OF DEAERATOR FOR OXYGEN STRIPPING DURING TEST OF APRIL 10, 1964



T = 122 °F, P = 1.6 psia
Brine Flow = 488,000 lbs/hr
Outlet Vapor Flow = 1050 lbs/hr
O_2 In Inlet Brine = 6.5 ppm
O_2 In Outlet Brine = 0.01 ppm
pH Of Inlet Brine = 4.0

FIG. IV– C –9

OPERATING CONDITIONS OF DEAERATOR FOR CO_2 STRIPPING DURING TEST RUN OF APRIL 10,1964



T = 122°F , P = 1.6psia

Inlet Brine Flow = 488,000lbs/hr

Outlet Vapor Flow = 1050 lbs/hr

CO_2 In Inlet Brine 92 ppm

CO_2 In Outlet Brine 2.8 ppm

pH Of Inlet Brine 4.0

atmospheric O_2 into the brine system at any point downstream from Effect III makes airtight gasketted joints and pump shaft seals a major factor in maintaining a low concentration of dissolved O_2. After the O_2 inleakage has been reduced to a practical minimum, as is apparently true in the Freeport Conversion Plant, and after the deaerator successfully maintains the O_2 content of the brine to the neighborhood of 0.01 parts per million, then the emphasis of effort can be on a further reduction of the dissolved O_2 content by chemical means.

Arriving at a practical design value for residual total CO_2 in the brine leaving the deaerator is more difficult than for O_2, considering the following facts:

(1) No operating data on CO_2 removal by commercial deaerators is available.

(2) The 90 to 100 parts per million CO_2 concentration with which the Conversion Plant is concerned with is almost never encountered by commercial power-house deaerators.

(3) Even though a value of zero parts per million CO_2 is ideally desirable, industrial deaerators for which data is available seldom attain a value as low as 1.0 parts per million total CO_2.

A value of 0.5 parts per million CO_2 has been arbitrarily used for design purposes, even though it will be considered fortunate if values between one and two parts per million CO_2 are actually realized in the deaerator.

The conditions encountered in this deaerator (refer to Figures IV-C-8 and IV-C-9), both existing and in the proposed cases, are good examples of a type of situation described by Sherwood and Pigford(46), where the ratio of liquid mass velocity to gas mass velocity is very high. Under these conditions, the actual HTU values, based on liquid-film resistance, are much higher than normal, sometimes exceeding six feet or more. The conditions prevailing inside the stripping column in such a case fail to achieve countercurrent action, since the relatively feeble upward flow of gas is induced to reverse its direction in places by the much greater momentum of downward flowing liquid.

The ratio of liquid mass velocity to gas mass velocity (L/G), is 490:1 in the present deaerator and will be about 720:1 in Case II. Hence, it is concluded that the deaerator is subject to the difficulties of the situation just described. The use of a type of packing having as great a void volume per cubic foot as possible will minimize the troubles just described, but will definitely not eliminate them entirely.

Increasing the flow of leaving vapor will improve the efficiency of packing utilization, at the expense of heat economy. Decreasing the flow of leaving vapor and increasing the packed height will conserve heat, but will allow greater deviation from countercurrent conditions and poorer packing efficiency. Although it is doubtful that the deaerator will operate with greater than one transfer unit, the difficulties encountered are inherent in the terminal conditions imposed on it, and do not reflect either poor choice of type or design.

After the packing was removed from the deaerator on June 10, 1964, samples of effluent brine obtained by operating personnel during operation without packing showed no detectable O_2. This fact indicates that the conditions for O_2 stripping from boiling brine by the use of steam are considerably more favorable than predicted from extrapolated data obtained by air stripping. The active transfer area of the three-inch Raschig ring packing was approximately 9000 square feet. This was replaced by only an estimated 735 square feet of spray droplet surface area. This value is based on an estimate by Spray Engineering Company of a 5200-micron average droplet size for the eight-inch Sprayco nozzle in the deaerator. The required transfer area, based on extrapolated literature values for air stripping, is approximately 3800 square feet. Apparently there is very appreciable transfer area in the steam bubbles during ebullition.

Even though the present deaerator is able to reduce the O_2 content of brine to 0.01 part per million by operating without packing, its performance in CO_2 stripping is still uncertain at this time. Therefore, the theoretically calculated amounts of packing as shown in Table IV-C-I are being recommended.

Relocation of the deaerator has been considered. It is concluded that the present location is proper. This conclusion is based on the following points:

(1) Moving the deaerator further downstream would expose more upstream piping and heat exchangers to attack by dissolved O_2 and to possible carbonate scaling.

(2) Relocating to operate at a higher temperature means using higher pressure steam for stripping, and is contrary to the interests of heat economy. Relocating to operate at a lower temperature, say to ambient, may result in a greater packing requirement.

For the normalized plant, consideration has been given to separating the decarbonating function from the deaerating function by installing two separate stripping columns. The proposed decarbonator would be located upstream from the proposed deaerator at the equivalent location of the existing deaerator in the Freeport plant. It would operate at about 50°C (122°F), at atmospheric pressure, and employ approximately 110 cubic feet of air per minute to strip the acidified sea water to a residual total CO_2 content of one part per million. It would be six feet in diameter by 24 feet high and contain a ten-foot depth of packing. The pH of the effluent brine would be increased to 6.0 and the brine would pass through the 300-series heat exchangers to the first point that the temperature exceeds 212°F. Here, a commercially available deaerator would be located to reduce the expected four parts per million O_2 content to approximately ten parts per billion, and to reduce the one part per million residual CO_2 content to, say, 0.1 part per million, after which the pH of the brine is increased from 6.0 to about 7.5.

This scheme is not being recommended at this time for the normalized plant for the following reasons:

(1) Insufficient knowledge of the availability of commercial-type deaerators of materials of construction to resist the corrosive properties of sea water at pH = 6.0 and at temperatures in excess of 212°F.

(2) Sufficient confidence that the present type of deaerator in the Freeport plant in its equivalent present location can perform satisfactorily.

The scheme just mentioned should be given further consideration for the normalized plant only if the existing deaerator in the Freeport plant fails to consistently maintain a level of one to two parts per million of total CO_2 in the effluent brine after the recommended packing change has been made and after the operational suggestions of Section V-A-2 have been carried out.

C. Deaeration Design

2. Estimate the Efficiency of Other Types of Packing

The situation to be minimized in the present deaerator is the failure of the packing to permit countercurrent action. The major factors to be considered here are low resistance to gas flow imposed by the packing per unit of packing height and the ability of the packing to maintain good liquid distribution. A quantitative measure of the resistance to gas flow of a particular packing, is the "packing-factor" C, which in turn, is a function of the free volume. The relative gas-flow capacities of two packings vary inversely as the square root of the ratio of the packing factors for equal pressure drops and liquid velocities:

$$\frac{Q_1}{Q_2} = \sqrt{\frac{C_2}{C_1}}$$

where:

Q_1 and Q_2 represent the gas flows through the packing per unit cross section at a given pressure drop for two different types of packing, respectively;

C_1 and C_2 are the packing factors of the two types of packing, respectively.

Hence, a packing with a low packing factor is desirable.

Ceramic Raschig rings have poor liquid-redistribution characteristics, and as shown in Table IV-C-IV, have a high packing factor. Two-inch steel Pall rings have the lowest packing factor listed and have fairly good liquid-redistribution characteristics, but would be subject to corrosion in this environment. The choice would be either Maspac FN-90 of polystyrene or polypropylene, or plastic Pall rings, with preference given to Maspac in view of the slightly more favorable packing factor and the more complete knowledge of its liquid-redistribution characteristics.

No difficulty is foreseen with loading or flooding of the packing in any of the proposed revised conditions mentioned. With the highest liquid rate, which is 26,000 pounds per hour per square foot in Case II, the gas rate which will cause flooding is about 450 pounds per hour per square foot. This is more than eight times as much as the expected gas rate in the deaerator.

Difficulty might be encountered in Case II at the packing support plate unless the latter is provided with a large fractional free area. A "Gas Injection" support plate is recommended. The U. S. Stoneware Company offers a reinforced-plastic support plate with free areas greater than 80 per cent(53).

TABLE IV-C-IV

COMPARISON OF CERTAIN PROPERTIES OF VARIOUS TYPES OF PACKING

Packing Type and Size	Free Volume, %	Packing Factor	Surface Area, sq ft/cu ft	Ref.
2-in. Raschig rings - ceramic	75	75	28	(27)
2-in. Raschig rings - steel	92	57	31	(27)
1-1/2-in. Berl saddles - ceramic	75	76	44	(27)
2-in. Intalox saddles - ceramic	79	42	36	(27)
1-in. Tellerettes - polyethylene	87	57	N.A.	(27)
2-in. Pall rings - steel	94	17	37	(27)
2-in. Pall rings - plastic	91	24	31	(27)
2-in. Pall rings - ceramic	74	44	29	(52)
3-3/4-in. Maspac FN-90 (polystyrene)	92	20	25	(14)

C. Deaeration Design

3. Effect of Deaerator Performance on Condensation Rates and pH of Product Water

The conditions existing inside the tubes of the heating elements of the various evaporator effects enable the latter to act as efficient decarbonators and deaerators, even though the flows of brine and steam are not countercurrent. The brine is spread out in a thin flowing film in contact with turbulent vapor. If we assume that the conditions at the interphase area inside a tube approximate those existing inside Raschig-ring packing, then a K_L value can be calculated from an extrapolated K_La value based on the data shown in Tables IV-C-II and IV-C-III. The assumption is made that the resistance of the liquid film is controlling. Using this calculated K_L value, we can then compute the amount of CO_2 transferred from the liquid phase to the vapor phase for various residual CO_2 contents and pH values of the effluent brine from the deaerator.

The calculation mentioned above was made on the bases of: four parts per million total CO_2 in brine leaving deaerator; pH of brine leaving deaerator = 6.7 measured at $25^{\circ}C$ and 6.05 at $232^{\circ}F$; brine flow to Effect I = 490,000 pounds per hour; and vapor from Effect I = 29,900 pounds per hour. The value of K_L at $232^{\circ}F$ was calculated to be 1.77×10^{-3} pound CO_2 per hour per square foot per part per million CO_2. The conclusion was that under the above conditions, there is enough transfer area in Effect I to transfer between 95 per cent and 98 per cent of the total CO_2 from the brine to the vapor phase.

Gravimetric CO_2 determinations run on samples of brine to and from Effect I and on the vapor from Effect I are not in exact agreement with the above result. The analytical results indicate that about half of the CO_2 in the brine is transferred to the vapor phase in Effect I when the brine pH is 6.8. Whatever the value actually is, it will not vary appreciably over a range of initial CO_2 concentrations, say from 0.5 per cent to 6.0 per cent. In the following considerations the value has been taken as half of the total amount of CO_2 present in the brine.

If the total weight of vapors from Effect I were condensed under static conditions, the liquid produced would have an equilibrium pressure of CO_2 (P_{CO_2}) equal to about 3000 times the partial pressure of CO_2 in the original vapors (i.e., 0.147 atmosphere and 47×10^{-6} atmosphere, respectively, for four parts per million CO_2 in vapor). Due to this fact, the initial vapors condensing on the tubes of the heating element of Effect I leave behind a "blanket" or film of CO_2 around the condensing surfaces. This film increases in CO_2 concentration as H_2O condensation proceeds as well as in thickness due to retrograde diffusion of CO_2 molecules. This situation continues until the partial pressure of the CO_2 in the film around the condensing liquid is high enough to transfer CO_2 to the liquid at the same rate the CO_2 is entering the heating element. When this condition is reached, the rate of heat transfer from the tube surface is usually reduced to a small fraction of its normal value by the resistance of the CO_2 film. Unless enough of this CO_2 (along with N_2 and O_2) is continuously removed by a bleed stream, continued operation of the condenser is impractical. The total, absolute amount of CO_2 and other "non-condensables" responsible for the "choking-off" of the heat transfer can be very small. Hence, the quantity of non-condensables to be removed in the bleed stream can be small, depending upon the initial, entering concentration in the vapors upon the total pressure, and upon the concentration leaving in the condensed liquid.

Even though the absolute amount of non-condensables required to be removed from a heating element can be quite small, the quantity of steam required in the bleed stream can be appreciable. This represents a lowered heat efficiency of the plant. The only information available to the Conversion Plant operatin personnel about the flow of bleed steam is that when the condensation rate decreases, the flow of bleed steam ("vent stream") is too low. There is no way of knowing at how much more than the correct value the flow of bleed steam is being held.

The above considerations show how the residual CO_2, and other non-condensables in the deaerator effluent interfere with heat transfer by gas-film resistance.

The residual CO_2 in the deaerator effluent can also obstruct heat transfer by scale formation. If the pH and the gross CO_2 concentration are both sufficient high, then, as the brine is heated inside heat-exchanger tubes or inside evaporator tubes, it loses dissolved, free CO_2 as a result of the increase of P_{CO_2} with temperature. This, in turn, causes a shift of equilibria in the CO_2-H_2O-$Ca(OH)_2$ system in the brine, resulting in the precipitation of $CaCO_3$ as a scale on the exchange surface. This process has been adequately discussed by McCutchan and Glater(29), and is summarized by:

$$Ca^{++} + 2HCO_3^- \longrightarrow CaCO_3 + CO_2\ (g) + H_2O.$$

No difficulty with calcium carbonate scale formation should be encountered until gross CO_2 concentrations of above the range of 40 parts per million CO_2 (= 45 parts per million $CaCO_3$) at a pH of 7.0 in the deaerator effluent are reached. This can be deduced from Professor Langelier's diagram(32), and is more fully discussed under Section V-A-2.

The pH and the residual gross CO_2 concentration in the deaerator effluent also have a strong effect on the pH of the product water. The exact, quantitative relationship cannot be developed here due to lack of the necessary synoptic plant operating data, including the CO_2 concentration in the condensed water from each effect. A knowledge of the CO_2 partial pressure in close proximity to the condensing surfaces of the various effects would enable the calculation of the amount of CO_2 transferred from the vapors to the condensing water in each effect. The samples and operating data which are available are bases for the following semi-quantitative conclusions: (a) when the deaerator pH is about 6.7, measured at 25°C in air, and when its residual gross CO_2 content is four to eight parts per million, then between one-quarter and one-half of the CO_2 is transferred from the brine to the vapors leaving Effect I; (b) under the same conditions, about one-third of the total CO_2 leaving the deaerator appears in the final saline concentrate from Effect XII; (c) under the same conditions, about one-third of the total CO_2 leaving the deaerator appears in the product water as free CO_2.

The statement of conclusion (c) above is based on three samples of product water to Freeport which by gravimetric CO_2 analyses, showed four to eight parts per million CO_2 in excess of total alkalinity. Analyses of samples of product water to Dow also showed presence of free CO_2.

The presence of dissolved, free CO_2 in the product water increases the concentration of hydrogen ion (decreases its pH value) according to:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

The theoretical pH values, measured at 25°C for several concentration levels of dissolved, free CO_2 are listed in Table IV-C-V. The values apply to pure water of zero alkalinity containing no other impurities capable of hydrolyzing and dissociating.

The presence of dissolved, free CO_2 in water creates an environment that is especially corrosive to plain steels for a combination of three reasons. The increase in hydrogen-ion concentration permits the oxidation of the base metal at an increased rate:

$$Fe^o + 2H^+ \longrightarrow Fe^{++} + H_2$$

The lower hydroxyl-ion concentration permits attack by any dissolved O_2 to proceed at an increased rate by lowering the concentration of the cathodic reaction product:

$$O_2 + 2H_2O \longrightarrow 4OH^- - 2e^-$$

The nature of the corrosion product, either $Fe(HCO_3)_2$, Fe_3O_4, or a mixture of both, is of such physical consistency that it fails to protect the anodic areas and thus maintains favorable reaction kinetics (see Section V-B-1-b).

The foregoing considerations regarding dissolved free CO_2 in fresh water, also apply to the brine. If, because of poor deaerator efficiency, the residual CO_2 content exceeds the alkalinity maintained in the deaerator effluent, appreciable quantities of free CO_2 may exist in the brine.

A single sample obtained of the vapors from Effect I showed an order of magnitude value of 0.6 part per million by weight of elemental hydrogen, as determined

TABLE IV-C-V

VARIATION OF pH OF FRESH WATER WITH CO_2 CONTENT[1]

Free CO_2, ppm	HCO_3^-, ppm	Total CO_2, ppm	pH in situ at 25°C
0.5	0.09	0.59	5.61
1.0	0.13	1.13	5.48
2.0	0.19	2.19	5.34
4.0	0.27	4.27	5.19
8.0	0.39	8.39	5.04
16.0	0.54	16.54	4.89

[1] Calculated from values for K_1' presented by Hamer, et al(16)

by vapor-phase chromatographic analyses. The vapor rate from Effect I vapor body at the time the sample was obtained was approximately 20,000 pounds per hour. These figures indicate there is approximately 0.288 pounds of hydrogen generated per day between the deaerator and the vapor outlet from Effect I. If the only source of this hydrogen is hydrogen ion attack on steel, then as much as eight pounds of iron per day is being corroded by hydrogen-ion attack between the deaerator and the outlet to Effect I. Elemental hydrogen was also present in the vent streams from Effect II and Effect III. If the residue of the magnesium anodes installed during March, 1964 in certain of the heat exchangers was still active at the time of sampling, the corrosion rate of the steel surface involved will not be quantitatively equivalent to the amount of hydrogen detected.

The installation of impressed-current anodes in the head space of the 300-series heat exchangers will minimize corrosive attack on the heads and tube-sheets by the hot brine. A reduction in the rate of corrosion will result from their use regardless of the value of the existing rate.

If, as indicated by Langelier's diagrams(32), the pH of the effluent brine from the deaerator could be maintained at, say 7.6 instead of at the present 6.7, then a threefold advantage would result: the corrosion rate in the entire brine system would be lowered; the product water would be rendered less corrosive; a very slight improvement in heat efficiency would be obtained as a result of a decrease in the required vent stream rates.

C. Deaeration Design

4. Availability of Commercial or Standard Deaerators

a. Conclusions

(1) Commercial deaerators of standardized design are available from manufacturers of power-house equipment in the water-rate size in question to deoxygenate fresh water to levels of 0.007 part per million of dissolved O_2. However, they are not immediately adaptable to the existing Freeport Conversion Plant or to the normalized plant for the following reasons:

(a) The type guaranteed to reduce the dissolved O_2 content to seven parts per billion is designed to employ stripping steam at above-atmospheric pressures.

(b) The type guaranteed to reduce the dissolved O_2 content to seven parts per billion would have to undergo considerable revision in materials of construction to withstand the corrosive properties of hot sea water at four pH.

(c) No information is available from manufacturers about the decarbonating efficiency at the high concentration levels of free CO_2 in the inlet brine in question.

(2) Three manufacturers of deaerators of the steam-jet "tray-type" were asked to submit modified designs and to quote approximate prices of lined deaerators. All three felt that their knowledge of the performance of this type of deaerator under the conditions in question was insufficient to permit either a performance assurance or a definitive price quotation. All three agreed that the additional cost to line the deaerator would be considerable.

(3) A standardized vacuum deaerator is commercially available in sizes to handle the brine flows in question. These are of the same general type as the existing deaerator in the Freeport plant. Their installed cost is in the same range as that of the Freeport deaerator, and the guaranteed O_2 content of the effluent is not as low as for the tray type.

b. Discussion

Commercial deaerators used in the steam-power industry are of two general types: vacuum and steam-jet "tray" type. The vacuum type consists physically of a vertical cylindrical tower, usually packed either with Raschig rings or slats. The feed water is sprayed through a nozzle into the top of the tower and passes down over the packing. A vacuum of 28 to 29 inches of Hg is usually employed. Steam may be injected into the base of the tower. Its action depends upon lowering the partial pressure of O_2 in the atmosphere of the tower to a low value. The packing is employed to provide more exchange surface than the surface area of the spray droplets affords. This type of deaerator offers little possibility for countercurrent action. The O_2 concentration in the deaerated effluent is usually in the 0.2 to 0.4 part per million range when operating at 28.5 inches of Hg vacuum and ambient temperature.

The steam-jet, tray-type deaerator actually embodies two types: the steam-jet atomization, and the tray design. This type operates at above-atmospheric pressure and at temperatures near saturation. The inlet water is jet-atomized into a steam atmosphere where it loses most of its dissolved O_2 through the surface of the atomized droplets. The water then passes over a series of horizontal, staggered trays, countercurrent to the flow of fresh steam. Here, conditions permit countercurrent action, or "staging", so that the O_2 content can be reduced to lower values than with the vacuum deaerator. Oxygen levels as low as five to seven parts per billion are claimed for this type of deaerator.

The steam inlet and exhaust connections in the tray-type deaerator are sized for super-atmospheric steam, as is the space between the trays. The pressure drop across the nozzle of the atomizer is usually greater than 0.5 pound per square inch.

Table IV-C-VI compares design and operating conditions of the deaerator of the Freeport Conversion Plant with a commercially available, standardized, vacuum deaerator operating in a power house.

TABLE IV-C-VI

COMPARISON OF DEAERATOR AT FREEPORT CONVERSION PLANT WITH COMMERCIALLY AVAILABLE VACUUM DEAERATOR

	Freeport Conversion Plant	Commercial Unit
Total Height, ft	42	24
Diameter, ft	6	7
Total Volume, cu ft	1,160	925
Cross Sectional Area, sq ft	28	38
Packed Height, ft	16	12
Type Packing	Rings	Rings
Volume of Packing, cu ft	441	462
Total Water Flow, gpm	1,000	1,200
Wetting Rate, gpm/sq ft	36	31
gpm/cu ft Packing	2.26	3.12
Operating Pressure, psia	1.5	0.75
Liquid Temperature, °F	122	75
Steam Temperature, °F	126	None used
O_2 in Inlet Water, ppm	7 to 8	7 to 8
O_2 in Outlet Water, ppm	0.01	0.10
Installed Cost	$20,000	$20,000

C. Deaeration Design

5. Recommendation for Future Research on Deaeration and Decarbonation

a. The present investigation has revealed that although adequate design data exists in the literature for desorbing O_2 and CO_2 from water by air, no data could be found for desorbing O_2 and CO_2 from water with steam. Conditions for desorbing with steam are apparently more favorable than can be predicted from air stripping data. It is recommended that basic design data for deaerating and decarbonating sea water by the use of steam be obtained experimentally.

b. Certain repetitive mathematical processes are necessary in computing both equilibrium conditions and reaction rates when only incomplete terminal conditions are known. It is recommended that computer programs be established for solving the mathematical expressions necessary for computing equilibrium conditions and mass-transfer rates in the system: sea water - CO_2.

D. Evaporator Design

1. Effect of Tube Diameter

The over-all heat-transfer coefficients calculated for various tube diameters and lengths are compared in Figure IV-D-1 to the clean over-all coefficient for two-inch, 24-foot tubes for each effect. The over-all coefficients were computed by Houston Research Institute, Inc. (HRI) using the fouling factors as indicated on page 17 of Appendix A. The effect that changing the tube diameter and length has on the heat-transfer area requirements is presented on page 36 of Appendix A. The heat flux for various tube sizes as a function of effect number, Figure IV-D-2, was taken from HRI results. This figure indicates that from a heat-transfer consideration, the two-inch, 24-foot tube is the best selection for the first eleven effects and that a larger tube would be favored in Effect XII. However, economic evaluation of the effects with various tubes indicates that there is no advantage in changing to the larger tube sizes. For the present plant operation, Effect XII with two-inch or four-inch, 24-foot tubes was estimated at $35,000 while with three-inch, 20-foot tubes it would cost $36,900. The estimates for the cost of Effect XII for the 300°F operation were, with two-inch, 24-foot tubes, $51,700; with four-inch, 24-foot tubes, $55,600; and with three-inch, 20-foot tubes, $58,300. The cost figures given above are for the vessel constructed and delivered to the site but not installed.

TABLE IV-D-I

EVAPORATOR DESIGN COMPARISON

Effect No.	Area, sq ft[3] Present Plant	Proposed Plants[1] 275°F	 300°F	Normalized[2] Plant
I	6,154	6,841	7,944	5,313
II	5,865	4,722	5,484	3,768
III	5,865	4,461	5,174	3,768
IV	4,810	4,309	5,004	3,768
V	5,338	4,195	4,872	3,768
VI	6,719	4,293	4,985	3,768
VII	5,338	4,254	4,940	3,768
VIII	6,154	4,300	4,994	3,768
IX	5,865	4,744	5,509	3,768
X	5,338	5,329	6,189	3,768
XI	6,983	6,787	7,882	5,313
XII	7,033	8,942	10,384	6,556

[1] Required area based on heat load for effect
[2] Design area
[3] All cases used 2-inch, 24-foot, 16-BWG tubes

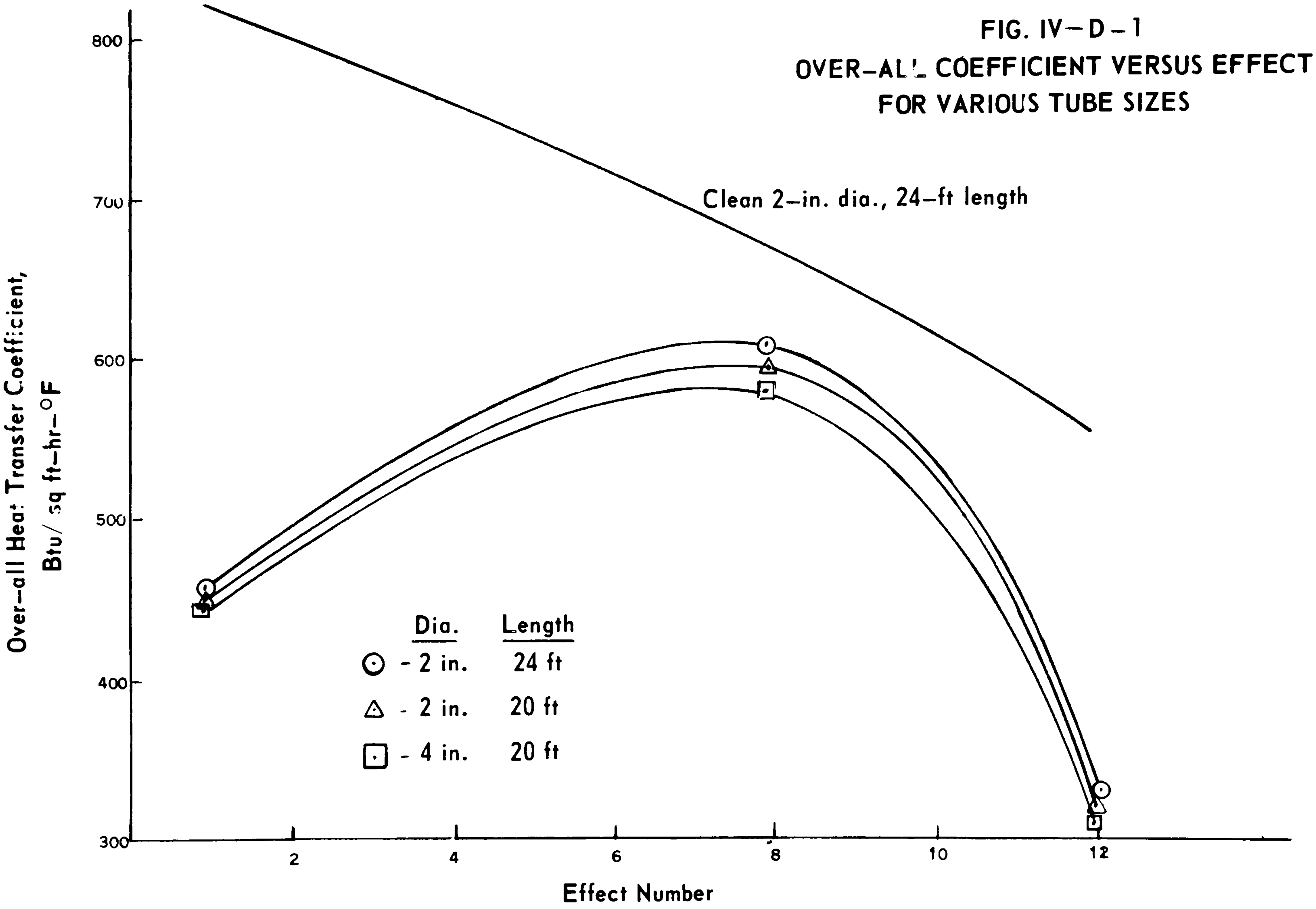


FIG. IV–D–1
OVER-ALL COEFFICIENT VERSUS EFFECT
FOR VARIOUS TUBE SIZES

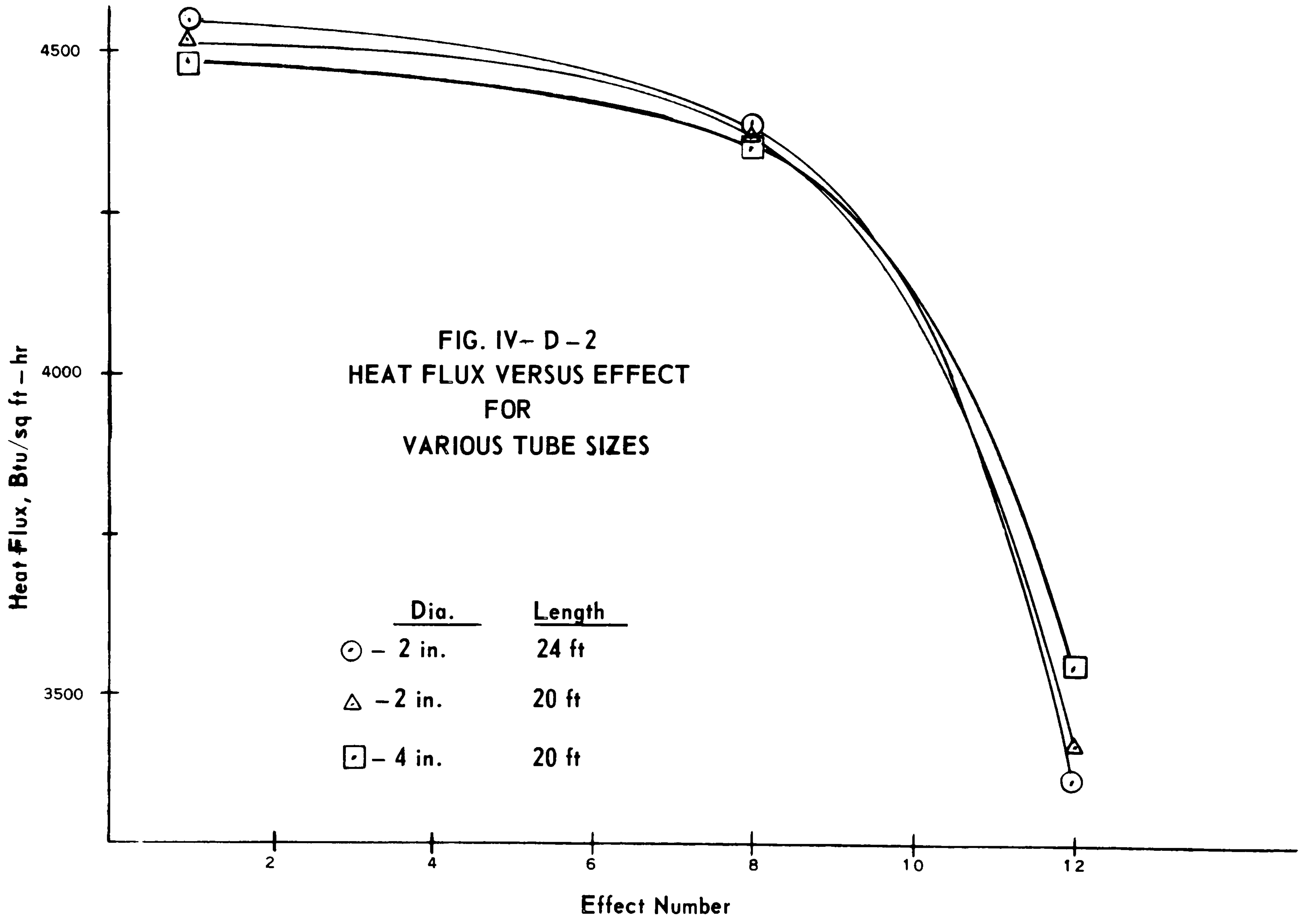


FIG. IV– D – 2
HEAT FLUX VERSUS EFFECT
FOR
VARIOUS TUBE SIZES

D. Evaporator Design

2. Effect of Recirculation

A study was made by HRI, (page 45 of Appendix A) to determine the effect of recirculation on the required heat-transfer area in Effects I and XII. In Effect I, recirculation of the brine was found to produce a slight reduction in area requirement. However, this reduction was not large enough to justify any change in operation. Brine recirculation in Effect XII increased the required heat-transfer area. The recirculation of brine in Effect XII also increases the pump requirement and operating cost of the plant. There is no justification for recirculation from economic or heat-transfer considerations. Justification for recirculation must be on the basis of scale prevention. The brine-feed distribution was improved by recirculation, but it is believed that the weir inserts can handle the distribution without the recirculation.

SECTION IV. GENERAL PLANT DESIGN

D. Evaporator Design

3. Influence of Maldistribution

The influence of maldistribution, (page 46 of Appendix A) was found to be more critical in Effect XII than in Effect I. An average tube effluent of 90 per cent saturation reached saturation with 40 per cent of normal flow through a tube in Effect I while saturation would be reached with 60 per cent of normal flow through a tube in Effect XII. The distributor plates used at present in the plant when operating without plugged areas seems to be an adequate solution to the problem. The addition of weir inserts give added assurance of good distribution even when areas of the plates are plugged off.

D. Evaporator Design

4. Recommendation

From this study, it is believed that additional work should be undertaken to determine the optimum height and configuration for the weirs.

E. Entrainment-Separator Design

1. Evaluation of Performance of Existing Separators

The purpose of an evaporator-effect separator is to provide for the removal of liquid droplets from the vapor produced. The liquid droplets may become entrained in the vapor passing down through the tube center because of: a rough tube entrance section resulting in liquid being thrown into the center vapor space; an extremely rapid, localized boiling rate; and an excessively high relative velocity between vapor and liquid in two-phase flow resulting in droplets being sheared from the falling film.

The third cause may be heightened by scaling of the tube.

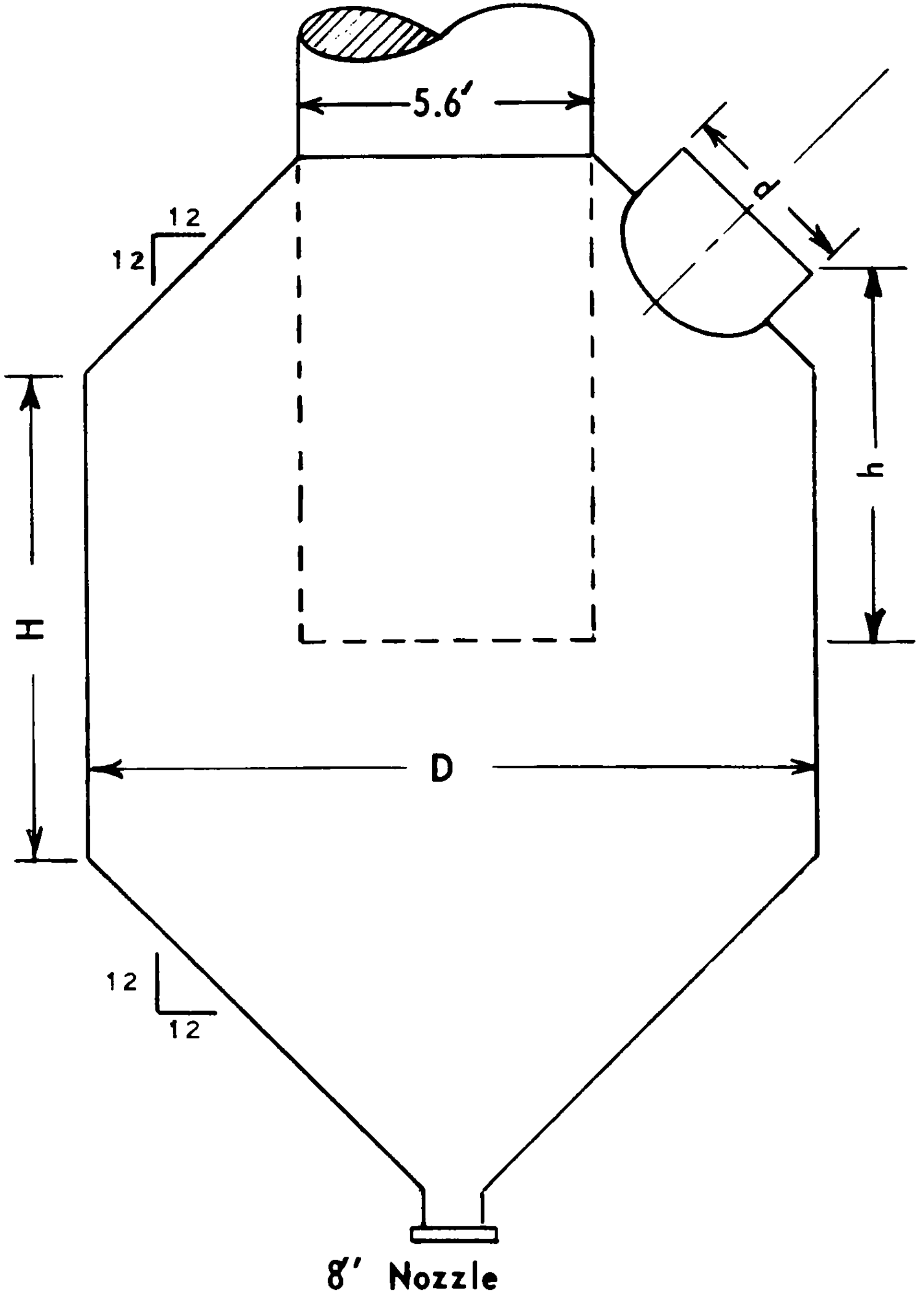
The chief faults of entrained brine in saline-water evaporation are product contamination and increased corrosion in product-water lines. The U. S. Public Health Service's suggested maximum dissolved solids content of water for human consumption is 500 parts per million.

The separators in the Freeport plant reduce brine entrainment by passage of the vapor-liquid mixture into an enlarged shell below the tubes. The resulting reduction in vapor velocity permits droplets to settle out by gravity. As the vapor turns 180 degrees to pass to the next effect, the droplets are separated by inertia from the vapor. The dimensions of the separator bodies are shown in Figure IV-E1-1 on the following page.

Brine entrainment in Freeport-plant product vapor is monitored by reading the electrical conductivity of the combined condensate from each set of steam chest and 300-series condenser. This is related to salinity by a curve furnished by Industrial Instruments, Inc. It gives the salinity in the range 2.0 to 40 parts per million as 0.694 times the specific conductance in micro-mhos at 20°C. Plant instrumentation includes correction for condensate temperature. Available curves of the specific conductance of aqueous NaCl solutions remain linear in the 1.0 to 300 parts per million range, so it is likely the sea-water curve could be extended to this concentration also.

FIG. IV-E1-1
SEPARATOR DIMENSIONS

Effect Number	D Cylindrical Shell Dia., ft	H Cylindrical Shell Ht., ft	d Vapor Outlet Dia., in.	h Vapor Annulus Ht., ft
I	10	10	24	4.52
II	10	10	24	4.81
III	10	10	24	4.29
IV	10	10	24	5.83
V	10	10	24	5.83
VI	10	10	24	5.83
VII	10	10	26	5.65
VIII	12	8	28	6.47
IX	12	8	32	6.47
X	14	6	34	5.33
XI	16	6	36	7.10
XII	18	6	42	8.49



The conductivity of the product from each effect and the Dow and Freeport municipal product water is logged at four-hour intervals. A review of plant data taken over the past 15 months indicates the present separators are performing satisfactorily. Product from each of the first nine effects has run below seven parts per million consistently. Effect X product has run about 16 parts per million and Effect XI product consistently below four parts per million. Effect XII product varied from seven parts per million to over 250 parts per million during the May 28, 1963, maximum-production run in which severe scaling of the effect occurred. It can be kept well below 100 parts per million providing the tubes are not allowed to become scaled.

Presentation of the typical vapor velocities in the separators helps to explain the above data. From the March 19, 1964 run, on which Figure III-A-1, the present plant heat and material balance was based, we find:

Effect Number	Vapor Produced, lb/hr	Superficial Vapor Velocity, ft/sec	
		Separator Shell	Annulus Around Effect Shell
I	27,948	1.88	2.74
II	28,619	2.18	3.18
III	27,526	2.51	3.66
IV	26,095	2.72	3.96
V	25,220	3.12	4.55
VI	24,748	3.59	5.23
VII	24,117	4.29	6.25
VIII	26,608	4.14	5.30
IX	26,823	5.32	6.81
X	26,456	5.33	6.35
XI	23,181	4.34	4.95
XII	23,618	5.82	6.45

This reveals where the changes in separator diameter occur. It also shows that the increase in separator diameter for Effect XI more than compensated for the increase in vapor specific volume and resulted in purer product than that from either Effect X or XII. It should be kept in mind that the result of a given amount of liquid entrainment becomes progressively worse from the first to the last effect because of the increasing brine concentration.

An article by A. D. Scheiman(40) provided another standard to which the effect separators could be compared. Data from the March 19, 1964 balance was required to calculate the vapor volumetric flow rate. Densities of the vapor and liquid streams were based on saturated vapor at the vapor head temperature and the brine samples taken. The suggested vapor velocity ratio value of 0.44 was used. The vapor rate for the last three cases exceeded the nomograph scale, so the diameter had to be calculated by the equation on which the nomograph was based.

		Present Plant Separator	
Effect Separator	Diameter from Nomograph, ft	Shell Diameter, ft	Vapor Annulus Hydraulic Radius, ft
VII	8.8	10.0	6.9
IX	10.3	12.0	9.4
XI	10.8	16.0	14.0
XII	12.4	18.0	16.3

In summary, the plant was designed to produce the one million gallons per day at less than 50 parts per million dissolved solids. It now easily produces water at less than half this value, and the present separators should be adequate for modest production increases.

E. Entrainment-Separator Design

2. Comparison of Existing Type and Wire-Mesh Type Separators

When the upward velocity of a vapor is too high to permit entrained droplets to separate by gravity, wire-mesh mist eliminators are beneficial. The droplets impinge upon the strands and flow down to wire junctions which act as gathering points. There they combine into larger drops which can fall free.

The previous section presents evidence that the entrainment separation being achieved by the plant separators is more than adequate. The possibility remains that the use of knitted-wire-mesh mist eliminators would permit a reduction in separator-shell size. Dow experience shows that provision should be made in such an installation to periodically spray wash the mesh to avoid excessive pressure drop due to fouling. The capital saved by separator-shell-diameter reduction thus must be balanced against not only the wire-mesh cost, but also the additional hardware and operating cost for periodic spray washing.

The calculation of an equivalent reduced-diameter, mist-eliminator-equipped separator was based on an article by O. H. York and E. W. Poppele(54). The paper presented the effect of liquid entrainment on allowable gas velocity. From the March 19, 1964 data, the product-water conductivity, brine-concentration factor, and densities of the vapor and brine were used to calculate the liquid-entrainment load. The load was low enough in all cases to give an allowable vapor velocity ratio of 0.4. In addition to the liquid and vapor properties, the allowable velocity ratio contained the void fraction and specific surface area of the mesh style under consideration. Curves were also presented from which the total pressure drop across the mesh, considering both the dry mesh and the liquid load, could be determined.

Table IV-E-I lists the results of the calculations. York Mesh Style 421 has over twice the specific surface of Style 931 and so provides better separation. Style 931 is designed for operation where the entrainmen is especially dirty or viscous, or where the liquid entrainment load is high.

TABLE IV-E-I

RESULTS OF REDUCED-DIAMETER SEPARATOR CALCULATIONS

Effect	Separator ID, ft	V, Superficial Vapor Velocity in Annulus, ft/sec	Reduced Diameter, ft	Resulting V, ft/sec	Type of York Wire-Mesh Screen	Calculated Allowable V with Screen, ft/sec	Pressure Drop Across Screen, psi	Liquid Superheat Loss, °F
IX	12	6.81	10	11.2	421	25.7	0.0073	0.07
					931	40.5	0.0031	0.03
X	14	6.35	10	15.2	421	29.9	0.0095	0.12
					931	47.2	0.0039	0.05
XI	16	4.95	12	9.9	421	32.9	0.0049	0.07
					931	51.9	0.0021	0.03
			10	16.2	421	32.9	0.0102	0.15
					931	51.9	0.0042	0.06
XII	18	6.45	14	11.5	421	41.9	0.0044	0.10
					931	66.0	0.0019	0.04
			12	16.8	421	41.9	0.0074	0.17
					931	66.0	0.0029	0.07

The allowable velocity with wire-mesh mist-eliminator use is frequently given as:

$$V = K\left(\frac{\rho_L - \rho_G}{\rho_G}\right)^{1/2}$$

where:

ρ_L = liquid density, lb/cu ft

ρ_G = gas density, lb/cu ft

K = a constant (0.35 in all usual applications)

V = allowable velocity, ft/sec

The more involved procedure presented in the York-and-Poppele paper was followed in this report since the value of K for the vacuum conditions in the separator was uncertain. Back calculation revealed that an equivalent K varied from 0.359 to 0.342 from separator IX through separator XII conditions for Mesh Style 421, and similarly from 0.565 to 0.539 for Mesh Style 931.

E. Entrainment-Separator Design

3. Economic Comparison of Separator Types

The maximum allowable vapor velocity from Table IV-E-I was used to calculate the minimum separator diameter permissible. Diameter calculations took into account the 2-1/2-inch wide wire-mesh support rings originally built into the separator and tube-shell circumference. The reduced-diameter separator cost was based on the use of a six-inch thickness of York Mesh Style 421, which would provide the best entrainment removal. Present separator height was maintained since the present vapor-annulus height was very close to the disengaging height recommended(40). Monel mesh and spray-washing hardware material were specified. The fabricated costs are:

Separator Number	Present Diameter, ft	Separator Cost	Reduced Diameter, ft	Separator Cost
IX	12	$ 7,170	8.67	$ 7,800
X	14	9,770	-	-
XI	16	12,320	8.93	7,860
XII	18	15,850	9.58	8,370

The wire mesh with its top and bottom grid comprised about $1000 of the cost of the reduced-diameter cases. Changing to the more open York Mesh Style 931 would reduce the cost by $470.

The reduced-diameter separator purchased cost becomes the more favorable one after Effect IX.

E. Entrainment-Separator Design

4. Conclusions and Recommendations

Though the capital cost estimates favor the use of wire-mesh mist eliminators in the last three separators if a new plant were built similar to the Freeport plant, the additional operating costs are difficult to estimate because of the uncertainty of the amount of fouling likely to occur. This would determine the washing-water usage, frequency, and whether a plant shut-down would be required to accomplish adequate washing.

Some observations concerning wire-mesh mist eliminator usage in saline-water evaporation were obtained. Wire mesh was apparently used successfully in the San Diego multistage, flash demonstration plant in which the entrained brine was about 1.7 times normal sea-water concentration. [Difficulty has been experienced with gravity separator at the Roswell, New Mexico vapor compression plant, which was corrected by wire-mech mist eliminator. Dissolved solids is about 6%. Dissolved-solids contents of this brine is also about 1.7 times normal sea water but the elemental composition is different.]

Observation of the Effect XII separator interior is best accomplished by shining a light through an observation port in the top 45-degree section of the body, and looking through another port in the vertical side. The top port glass is continuously washed with vapor and entrained brine, and only temporary heat from the light is sufficient to cause formation of an opaque film on the glass. Heavy salt deposits are observed on the tube shell at each shutdown. Since the shell contains the hotter steam from the previous effect, the deposit probably forms simply from the evaporation to dryness of entrained brine. The inner perimeter of a wire-mesh pad would be directly supported by this hotter tube shell.

Due to the above considerations, it is recommended that only the simpler and more trouble-free velocity-reduction type separators be used in LTV evaporation plants.

Only Effect XII shows any indication of possible excessive entrainment at higher production rates. Should this occur, the support rings built into each separator body should permit easy installation of a wire-mesh pad for trial operation. The coarser-woven York Style 931 in monel is recommended for this service.

F. Utilization of High-Pressure Steam Energy

The requirements of Effect I for the revised plant operations have eliminated the feasibility of using the high-pressure steam in any turbine-driven machine. The requirement of Effect I and the available steam is shown in Table IV-F-I. The steam available to the plant is 150-pound steam and is the same as would be available to the revised plants. Since the normalized plant has to produce its steam and is operating with the 300°F conditions in Effect I, other forms of energy are more economical for mechanical work.

TABLE IV-F-I

STEAM ENERGY UTILIZATION

Steam Required to Effect I	Operation		
	Present	275°F	300°F
Temperature, °F	241	288	316
Pressure, psia	25.427	55.8	84.7
Flow, lb/hr	31,250	44,868	56,347
Steam Guaranteed to Plant			
Temperature, °F	490	490	490
Pressure, psig	150	150	150

G. Materials of Construction and Corrosion

1. Heat Exchangers

a. Non-Ferrous Tubing

A Probolog was employed to evaluate the tubing. It is an eddy-current device which senses pits, holes, cracks, and changes in the tube-wall thickness. With one exception, the tubing is in good shape. This is heat exchanger 215 receiving raw sea water at ambient temperature. The tubes are aluminum brass. They are severely pitted on the first pass near the inlet nozzle, and these tubes will probably have to be replaced within six to 24 months. There is pitting in both passes and it is estimated that complete retubing will be required in three to four years. The pitting is caused by marine bio-fouling. Downstream of this unit, water temperatures are high enough to kill the fouling organisms.

There are three methods by which this fouling can be controlled: continuous chlorination to a chlorine residual of one-half part per million as determined by methyl-orange titration; periodic heating to 150°F or more obtained by temporary shutdown or crossover piping with a hotter downstream heat exchanger; and retubing with copper.

There are serious objections to chlorination. Water velocity in this unit is reported to be about 1.5 feet per second. Copper will maintain a protective film in ambient sea water up to two feet per second. If copper is considered, a few experimental tubes should be installed to make certain that copper will withstand the operating conditions.

Other heat exchangers Probologed were 301, 304, 311, 201, 211, and 214. These included Admiralty, aluminum brass, and 90:10 cupro-nickel. They were all in very good condition.

b. Discussion

Dow experience with aluminum brass and 90:10 cupro-nickel gives a life of 11 to 15 years.

There is no general thinning or attack. The greatest single cause of failure is the lodgement of shell fragments or other foreign bodies in the tubes. This creates local turbulence which destroys the protective film and causes perforation. Some shell fragments, small crabs, etc., were noted on the top tube sheets. There were also large thick flakes of rust from the piping and water boxes. Plant experience indicates that these interfere with operations and could cause trouble when lodged in a tube.

c. Steel Water Boxes

The water-box shells are corroding rapidly and dividing plates have to be renewed from time to time. This corrosion and that of the tube sheets can be completely and permanently arrested with impressed current. In general the water temperature is too high to make magnesium anodes practical. Impressed-current anodes of platinized titanium or titanium tipped with carbon or Durichlor Alloy are inexpensive and practical. Those used by Dow cost $6.00 each for materials and are easily assembled by any mechanic. They consist simply of a 1/4-inch diameter titanium rod ten inches long potted with epoxy resin into a 1-1/2-inch by one-inch pipe swage which is threaded into the vessel wall. The titanium rod is tipped with a one-inch diameter piece of Durichlor 2-1/2-inch long. Corrosion-engineering firms in Houston can, of course, supply all the necessary equipment and design. In addition to permanently protecting the water boxes and tube sheets, this will eliminate part of the rust-flake problem.

If impressed current is employed, all insulating gaskets now in the system must be removed. Currently they are serving no useful purpose. If they are not removed, there will be severe corrosion next to the gasket on the side nearest to the current source.

G. Materials of Construction and Corrosion

2. Evaporators

a. Non-Ferrous Tubes

Tubes in the first four effects were Probologed. The aluminum-brass tubes in Effect I were in "like-new" condition. Some experimental Type 304 stainless tubes in this effect showed moderate to severe pitting. This would be expected. The Admiralty tubes in Effect II showed some very slight pitting and some superficial layer-type dezincification. Aluminum brass in Effect III was in excellent condition. Probolog tapes on the 90:10 cupro-nickel indicated some pitting. Pitting in this effect was most unexpected. Removal of two tubes for metallurgical examination showed that the "pits" were actually dents and bruises of mechanical origin.

b. Steel, Upper Water Box

The thickness of selected portions, Table IV-G-2-I, were measured. The top water box and brine piping are suffering severe corrosion. Cathodic protection will not be effective in the top water box since the box is not full and its lower portion is masked by the distributor plate. The designers corrosion allowance of ten per cent has already been exceeded.

An investigation of coatings suitable for this service produced three (based on manufacturers' recommendations): Napko S 1670 S.T.P. Bakeline Phenolic, Carboline Phenoline 368, and Amercoat D-4 overcoated with 1741. Applied cost is estimated at $1.50 to $2.00 per square foot. Laboratory tests conducted by Dow indicate a life for these coatings of three to 12 months, depending on temperature. It would obviously be cheaper to replace this portion of the evaporators every three years than to employ these coating systems. This could probably be done for $2.00 per square foot. Coal-tar epoxies were considered but they will impart taste and color to the water.

c. Steel, Upper Tube Sheet

Severe pitting is occurring under the holes in the distributor plate. When measured in May, 1964, the loss in thickness amounted to about 1/4 inch. This corrosion will accelerate because of the recent installation of copper weir inserts into the top of the tubes. It will be further accelerated as corrosion lays bare the rolled-in portion of the tubes. These copper inserts preclude the application of impressed current below the distributor plate. An anode will protect only "what it can see".

A protective coating or "puttying up" the deep pits with some kind of mastic is not deemed advisable. In order to be successful, such an attempt would have to be 100 per cent perfect and near-perfection would be disastrous. All of the galvanic corrosion would be concentrated on any unprotected spots.

d. Weir Inserts in Top Water Box

In normally aerated sea water, crevice corrosion between the insert and the tube wall would occur. None was observed, doubtlessly caused by the low O_2 content of the water. This situation should be watched, however.

TABLE IV-G-2-I

THICKNESS MEASUREMENT OF SELECTED PORTIONS OF FOUR EFFECTS

EFFECT I

	Orig. Nominal Thickness	Lowest Reading
Top Water-Box Side Wall	0.375	0.280
Separator Top	0.70	0.710
Separator Side Wall	0.562	0.552
Bottom Cone Above Manway Neck	0.75	0.73
Manway Neck	0.50	0.49
8-in. Brine Discharge Weld Neck	1.125	0.900

EFFECT II

Top Water-Box Side Wall	0.375	0.322
Top Tube Sheet	2.75	2.56

EFFECT III

Top Water-Box Side Wall	0.375	0.248

EFFECT XII

Bottom Cone Above Manway Neck	0.625	0.620
Manway Neck	0.50	0.50
8-in. Brine Discharge Weld Neck	1.125	0.916

G. Materials of Construction and Corrosion

3. Piping

First perforation occurs in 18 to 36 months depending on temperature, turbulence in elbows, etc. In addition to shutdowns, operational trouble is caused by rust flakes and, as explained earlier, lodgement of these flakes in heat-exchanger tubes can cause some pressure drop.

Some test spools of reinforced plastic are in operation. There is serious objection to reinforced plastic due to its sensitivity to water hammer. This, together with its cost (three to five times that of steel), does not make it an attractive solution.

The condition of the 90:10 cupro-nickel tubes in the evaporators and heat exchangers clearly demonstrates that it would be a suitable piping material. However, when the cost of ten-gauge cupro-nickel is compared with that of steel, it was found to be about four times as expensive. The sea water and brine lines could be installed for $60,000 using steel pipe while the cost of installed 90:10 cupro-nickel pipe would be $242,000.

The non-ferrous alloys, including cupro-nickel, are subject to deposit attack, a form of O_2-concentration cell corrosion. In handling normally aerated sea water, it is necessary to maintain a velocity of five feet per second to avoid deposit attack. It is not known whether this would occur, or to what extent, downstream of the deaerator.

G. Materials of Construction and Corrosion

4. Pumps

Cavitation attack is a combination of mechanical and corrosion effects. The collapsing force of the bubbles has been estimated to be in the order of 50,000 to 60,000 pounds per square inch. This is sufficient to destroy the protective film on most metals. Without a film, corrosion can be very rapid. The instantaneous corrosion rate of bare iron in sea water has been estimated at one inch per year. Cavitation attack can be stopped or greatly reduced by cathodic protection but it is not very practical to apply it to pump impellers.

In cavitation tests in sea water, Cr-Ni stainless steel has proved itself to be superior to all other materials commonly available for pump impellers. Dow has standardized on 19-9 extra-low-carbon stainless steel and now has ten years' successful experience with it. (ASTM A 296 Grade CF8 extra-low carbon) It is greatly superior to Ni-Resist cast iron. The 19-9 is recommended for ambient sea water and for temperatures up to 120°F. Above this temperature it is believed that stress corrosion cracking will be a problem.

ASTM Specification A 296 Grade CN-7M (commonly known as "20 Alloy") is more resistant to stress-corrosion cracking than the other stainless steels, but it is not immune. It might be useful up to 200°F and would have better cavitation resistance than Monel Alloy 505, formerly known as S Monel, or Ni-Resist cast iron. Both stainless alloys can be repaired by welding.

Monel Alloy 505 should be used above 200°F. It is immune to stress-corrosion cracking. It is more resistant to cavitation attack than Ni-Resist but somewhat less so than the stainless steels. It cannot be welded.

Failures of the Monel shafts have not been a serious problem, but some trouble can be expected from corrosion-fatigue. This is brought about by imbalance of the impellers or hydraulic imbalance resulting from local corrosion of the casing. It has been Dow's experience that pump-shaft materials must combine a high yield strength and corrosion resistance. The ideal material is Monel Alloy K 500, and it was standard with Dow for many years. Extended and uncertain deliveries led to the trial and ultimate adoption of Armco 17-4 PH Temper H 1075 stainless steel, which has proved quite satisfactory. As the Monel shafts fail, replacement with this material is recommended for temperatures up to 200°F. Above this temperature, Monel Alloy K 500 is recommended for use with Monel Alloy 505 impellers.

G. Materials of Construction and Corrosion

5. General

The test-coupon survey made by the International Nickel Company with a variety of metals and alloys in general parallels actual experience in the Freeport Demonstration Plant and also parallels Dow experience. In this connection it should be pointed out that while type 304 stainless steel pitted severely, such behavior would not occur under the high velocity and turbulence incident to pump-impeller service. The unique combination of corrosion resistance and capacity to work-harden make the Cr-Ni stainless steels outstanding in resistance to cavitation attack in sea water.

G. Materials of Construction and Corrosion

6. Recommendations

Non-ferrous tubing in heat exchangers and evaporators is in excellent condition except in heat exchanger 215, where some damage has been caused by bio-fouling. Trial replacement with copper is recommended.

The heat-exchanger water boxes can be permanently protected with impressed current. This is recommended. Insulating gaskets should be removed if impressed current is employed. They are serving no useful purpose.

The evaporator top water boxes are suffering severe corrosion. Replacement of the walls, as necessary, appears to be the most economical expedient.

Pumps: 19-9 ELC stainless steel is recommended for impellers up to 120°F, "20 Alloy" stainless steel from 120°F to 200°F, Monel Alloy 505 over 200°F; pump shafts, Armco 17-4 PH Temper H 1075 for use with stainless impellers, and Monel Alloy K 500 for use with Monel Alloy 505 impellers.

Piping: It is more economical to replace the steel piping in the sea-water and brine lines, than to install 90:10 cupro-nickel pipe with a life of three to five times that of steel, but costing four times as much.

H. Mechanical Equipment Design

1. Description of Mechanical Equipment Construction and Design

The pump tabulations contained in Tables IV-H-I through IV-H-IV constitute the bulk of this section. Pump requirements for the various conditions of design have been tabulated for comparison with existing equipment. Table IV-H-I lists all of the existing pumps in service.

a. Pumps P-1 and P-2

These pumps are Johnston vertical-type, two-stage, impeller pumps. During the first two years of operation, cavitation erosion of the impellers has occurred. The size of these pumps, however, appears to be adequate for any of the various conditions of flow, and only the impeller material will need to be changed.

b. Deaerator Pump P-3

This pump is a Goulds Model 3755 and appears adequate for all conditions of flow. The original Ni-Resist impellers, although not recommended for sea-water and brine service, have not experienced any severe maintenance problems. We do recommend that this impeller be changed, and also that this pump be spared, as it is a critical item.

c. Deaerator Pump P-4, P-5, and P-5A

Considerable difficulties have been a continuing history of these pumps. It is our opinion that the particular problem of the cavitation caused by insufficient net positive suction head accounts for the vast majority of the troubles encountered with these impellers. The new P-5A, which has been installed since the plant was originally constructed, is a Worthington canned-type pump, but it is still rated as unsatisfactory, even at the existing plant conditions. In terms of capacity, this existing pump is adequate only for the increased flow at the 275°F Effect I temperature; but to satisfactorily operate in this service, we recommend that the longer can be installed on this existing pump.

d. Brine Pumps, P-11 through P-22

The Goulds Model 3189 pump, originally specified, is not the ideal pump for application as a brine pump in continuous operation. It cannot be equipped with a shaft sleeve, a desirable feature for this service. It should also be noted that the manufacturer limits the operating temperature of this pump to 180°F without cooling, 220°F with quench-gland cooling, and only 250°F with a water-cooled frame. At lower rated heads, all but P-11 and P-12 could possibly be utilized in the plant with an Effect I temperature of 275°F. Beyond that, the number of pumps that could be utilized diminishes to the point where it is more advantageous to have all pumps of the same model than to have two or three Model 3189's in the group of Model 3755's, or their equivalent.

e. Condensate Pumps

As all proposed alternate processes eliminate the need for a condensate pump for each effect, a discussion of this group of pumps is not necessary. A much larger P-41 is necessary, however, to handle the combined condensate streams.

f. Product Pumps P-44, P-50, and P-51

All of these pumps are of adequate design for their application. The impeller material is also suitable.

TABLE IV-H-I

Present Operating Plant

		Calculated Flow, gpm	Head, ft	Pump Selection	Impeller Material	Pump Cost	Horsepower Required	Motor Size	Speed, rpm
P-1 and P-2,	S.W.	4,000	22	Johnston 12" PO	Ni Resist	$7,353 ea.		50	1,150
P-3	S.W.	618	55	Goulds 6 by 6-9	Ni Resist	1,383		20	1,750
P-4 and P-5,	S.W.	880	270	Goulds 6 by 8-17	Ni Resist W/SS	4,418		125	
P-5A	S.W.	880	270	Worthington 15L82	316 SS	9,318		125	1,750
P-11	Brine	822	45	Goulds 3189 6 by 8-13	Ni Resist	1,224	12	15	1,150
P-12	Brine	764	45	Goulds 3189 6 by 8-13	Ni Resist	1,224	11	15	1,150
P-13	Brine	708	45	Goulds 3189 6 by 8-13	Ni Resist	1,224	10	15	1,150
P-14	Brine	652	45	Goulds 3189 6 by 8-13	Ni Resist	1,224	10	15	1,150
P-15	Brine	594	45	Goulds 3189 6 by 8-13	Ni Resist	1,224	9	15	1,150
P-16	Brine	541	45	Goulds 3189 6 by 8-13	Ni Resist	1,224	9	15	1,150
P-17	Brine	488	45	Goulds 3189 4 by 6-13	Ni Resist	957	8	10	1,150
P-18	Brine	422	45	Goulds 3189 4 by 6-13	Ni Resist	957	7	10	1,150
P-19	Brine	377	45	Goulds 3189 4 by 6-13	Ni Resist	957	6	10	1,150
P-20	Brine	323	45	Goulds 3189 4 by 6-13	Ni Resist	957	6	10	1,150
P-21	Brine	270	45	Goulds 3189 4 by 6-13	Ni Resist	957	6	10	1,150
P-22	Brine	223	45	Goulds 3189 4 by 6-13	Ni Resist	957	6	10	1,150
Spare	Brine	Replaces P-11, 12, 13, 14, 15, 16		Goulds 3189 6 by 8-13	Ni Resist	705	No Motor		
Spare	Brine	Replaces P-17, 18, 19, 20, 21, 22		Goulds 3189 4 by 6-13	Ni Resist	617	No Motor		
P-31	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-32	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-33	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-34	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-35	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-36	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-37	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-38	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-39	Condensate	65	70	Goulds 3755 1-$\frac{1}{2}$ by 2-9	BRZ 88-10-2	397	2.5	3	1,750

TABLE IV-H-I
(con't)

Present Operating Plant

		Calculated Flow, gpm	Head, ft	Pump Selection	Impeller Material	Pump Cost	Horsepower Required	Motor Size	Speed, rpm
P-40	Condensate	65	70	Goulds 3755 1-½ by 2-9	BRZ 88-10-2	$ 397	2.5	3	1,750
P-41	Condensate	65	70	Goulds 3755 1-½ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-42	Condensate	65	70	Goulds 3755 1-½ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
P-43	Condensate	65	70	Goulds 3755 1-½ by 2-9	BRZ 88-10-2	397	2.5	3	1,750
Spare	Condensate	Replaces P-31 thru 43		Goulds 3755 1-½ by 2-9	BRZ 88-10-2	224	No Motor		
P-44	Condensate	356	60	Goulds 3755 4 by 6-13	BRZ 88-10-2	877	8	10	1,150
P-47	S.W.	50	175	Goulds 3755 2-½ by 3-13	Ni Resist	1,037	19	15	1,750
P-50	Product	550	200	Goulds 3405 3 by 4-12		1,290	40	50	3,550
P-51	Product	425	200	Goulds 3405 3 by 4-12		1,134	33	40	3,550
P-52	Water	425	70	Goulds 3405 3 by 4-12		938	13	15	1,750

All pumps equipped with shaft packing.

New pump cost includes motor, base, and coupling, FOB factory.

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H. Mechanical Equipment Design

2. Technical Evaluation

a. General

The major considerations in the evaluation of all pumps with relation to their application under the various conditions of flow were as follows: net positive suction head requirements, choice of material for the impeller, head capacity requirements, and desirability of other improved mechanical features such as shaft sleeves and mechanical seals.

It should be noted that all new pump costs include appropriately chosen mechanical seals.

b. Pumps in Sea-water Service, P-1, P-2, P-3, and P-5A

As stated previously, Ni-Resist impellers are not suitable for this service due to their susceptibility to cavitation erosion. Otherwise, P-1, P-2, and P-3 have adequate head capacity curves for all conditions of flow in the various process alternatives. On the other hand, P-5A meets with some difficulty. For the first higher condition of flow (275°F Effect I temperature) represented in Table IV-H-II, the net positive suction head capability of the pump is inadequate, and it is recommended to extend the can an extra three feet for more available suction head. Considering P-3 is an unspared critical item in the process, it should be spared.

c. Brine Pumps, P-11 through P-22

The material for the impellers in these pumps must be either Monel 505 or Alloy 20, depending upon the temperature. According to the Goulds pump representative, impeller modification costs or new pump costs, as the case may be, would not be significantly different whether one specified Monel 505 or Alloy 20. On this basis, only the Monel need be considered, as it has the higher operating temperature capability. With an Effect I temperature of 275°F, the increase in flow is such to change the net positive suction head capability of P-11 and P-12 to the point that

TABLE IV-H-11

Plant Operating with Effect I Temperature of 275°F, Minimum Revisions

	Flow, GPM	Head, FT	Pump Required	Impeller and Shaft Sleeve Modification	Conversion Cost
P-1 and P-2, S.W.	3,650	22	Same	19-9ELC W/SS	$1,225 imp. mod. ea. pump
P-3 S.W.	1,195	55	Same	19-9ELC W/SS	600 imp. mod. ea. pump
P-5A S.W.	1,195	270	Same, but lower can 3'	Monel 505 or Alloy 20	4,500 mod.
P-11 Brine	1,190	35	Must have new pump, NPSH too low Must have new motor, 20 HP, 1,150 RPM		1,553
P-12 Brine	1,097	35	Must have new pump, NPSH too low Must have new motor, 20 HP, 1,150 RPM		1,553
P-13 Brine	1,008	32	Same	Monel 505	650 imp. mod. cost
P-14 Brine	921	33	Same	Monel 505	650 imp. mod. cost
P-15 Brine	834	35	Same	Monel 505	650 imp. mod. cost
P-16 Brine	750	35	Same	Monel 505	650 imp. mod. cost
P-17 Brine	655	35	Same	Monel 505 or Alloy 20	535 imp. mod. cost
P-18 Brine	588	35	Same	Monel 505 or Alloy 20	535 imp. mod. cost
P-19 Brine	512	35	Same	Monel 505 or Alloy 20	535 imp. mod. cost
P-20 Brine	435	35	Same	Monel 505 or Alloy 20	535 imp. mod. cost
P-21 Brine	359	35	Same	Monel 505 or Alloy 20	535 imp. mod. cost
P-22 Brine	287	35	Same	Monel 505 or Alloy 20	535 imp. mod. cost
Spare Brine	Replaces P-13, 14, 15, 16		Same	Monel 505	650 imp. mod. cost
Spare Brine	Replaces P-17, 18, 19, 20, 21, 22		Same	Monel 505 or Alloy 20	535 imp. mod. cost
P-41 Condensate	845	50	New pump required. All iron or bronze fitted with Type RO seal.		1,060
P-44 Condensate	152	60	Same	None	
P-50 Product	747	200	Same	New sleeves required	617
P-51 Product	249	200	Same	New sleeves required	

New pump cost includes motor, base, and coupling, FOB factory.
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other pumps be specified. Under conditions of minimum modification expense (Table IV-H-II), P-13 through P-22 would suffice for the higher flow requirements. Conversion to the Goulds Model 3755 pump or its equivalent is recommended, however (Table IV-H-III). For all other conditions of flow, refer to Tables IV-H-IV through IV-H-VII for the appropriate pump equivalent. Incorporating mechanical seals in all brine pumps would require some means of external flushing. A slight dilution would result, but with controlled addition of flushing product water by means of a throttle bushing, the effect would be negligible.

It will be noted that the head requirements for all of the brine pumps were lowered. In the original specifications, the estimated heads were too conservative. These specifications for higher-than-necessary heads magnified somewhat the tendency toward cavitation. It is felt, therefore, that the lower design heads are more realistic and will decrease some of the problems encountered with net positive suction head.

d. Condensate Pump P-41

The recommended pump is a Goulds Model 3755 6 by 6-9 or equivalent. This pump could be bronze or iron fitted, and would contain a mechanical seal, Durametallic Type RO or equivalent. It would be suitable for any of the conditions of flow specified.

e. Product Pumps P-44, P-50, and P-51

Incorporation of Type RO mechanical seals or equivalent is recommended. Materials in the existing pumps are suitable, but the size changes with the various conditions of flow.

TABLE IV-H-III

PLANT OPERATING WITH EFFECT I TEMPERATURE OF 275°F, RECOMMENDED REVISIONS

	Recommended Pump Equivalent	Pump Cost	Horsepower Required	Motor Size
P-1 and P-2, S.W.		$ 1,978 ea.		50
P-3 S.W.		693 imp. mod. ea.		20
P-5A S.W.		5,778 mod.		125
P-11 Brine	G 3755 8 by 8-11	1,553	17	20
P-12 Brine	G 3755 8 by 8-11	1,553	17	20
P-13 Brine	G 3755 6 by 6-9	1,376	12	15
P-14 Brine	G 3755 6 by 6-9	1,376	12	15
P-15 Brine	G 3755 6 by 6-9	1,376	10	15
P-16 Brine	G 3755 6 by 6-9	1,376	9	15
P-17 Brine	G 3755 6 by 6-9	1,307	10	10
P-18 Brine	G 3755 4 by 6-11 H	1,027	9	10
P-19 Brine	G 3755 4 by 6-11 H	1,027	7	10
P-20 Brine	G 3755 4 by 6-11 H	1,027	6	10
P-21 Brine	G 3755 4 by 6-11 H	1,027	5	10
P-22 Brine	G 3755 4 by 6-11 H	1,027	5	10
Spare Brine	G 3755 6 by 6-9	1,100	No Motor	
Spare Brine	G 3755 4 by 6-11 H	820	No Motor	
P-41 Condensate	G 3755 6 by 6-9	1,060	16	Use Old P-52 Motor
P-44 Condensate			5	10
P-50 Product			59	60
P-51 Product			23	40

New pump cost includes motor, base, and coupling, FOB factory.
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TABLE IV-H-IV

PLANT OPERATING WITH EFFECT I TEMPERATURE OF 300°F, RECOMMENDED REVISIONS

	Flow, GPM	Head, FT	Pump Equivalent	Pump Cost	Required Horsepower	Motor Size	Motor Speed, RPM
P-1 and P-2, S.W.	3,700	22	J. 12" PO	$1,978 ea. Imp. Mod.		50	1,150
P-3 S.W.	1,416	55	G 3755 6 by 6-9	640 ea. Imp. Mod.	23	25	1,750
P-4 and P-5, S.W.							
P-5A S.W.	1,416	270	W. 15M154-3	10,500		150	1,750
P-11 Brine	1,426	35	G 3755 8 by 8-11	1,553	17	20	1,150
P-12 Brine	1,306	35	G 3755 8 by 8-11	1,553	17	20	1,150
P-13 Brine	1,190	35	G 3755 8 by 8-11	1,486	16	15	1,150
P-14 Brine	1,078	35	G 3755 8 by 8-11	1,486	15	15	1,150
P-15 Brine	965	32.5	G 3755 6 by 6-9	1,307	9	10	1,150
P-16 Brine	861	34	G 3755 6 by 6-9	1,307	9	10	1,150
P-17 Brine	761	35	G 3755 6 by 6-9	1,307	8	10	1,150
P-18 Brine	658	35	G 3755 6 by 6-9	1,307	7	10	1,150
P-19 Brine	563	35	G 3755 6 by 6-9	1,272	7	7-½	1,150
P-20 Brine	466	35	G 3755 6 by 6-9	1,272	7	7-½	1,150
P-21 Brine	372	35	G 3755 4 by 6-11 H	958	5	5	1,150
P-22 Brine	282	35	G 3755 4 by 6-11 H	958	4	5	1,150
Spare Brine	Replace P-11-14		G 3755 8 by 8-11	1,210		No Motor	
Spare Brine	Replace P-15-20		G 3755 6 by 6-9	1,100		No Motor	
Spare Brine	Replace P-21-22		G 3755 4 by 6-11 H	820		No Motor	
P-41 Condensate	1,057	50	G 3755 6 by 6-9	1,314	17	20	1,750
P-44 Condensate	194	60	G 3755 4 by 6-13	300 Seal Mod.	6	10	1,150
P-50 Condensate	937	200	G 3405 6 by 8-8 G	1,367	67	60	3,500
P-51 Condensate	313	200	G 3405 3 by 4-12	300 Seal Mod.	27	40	3,500

New pump cost includes motor, base, and coupling, FOB factory.

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H. Mechanical Equipment Design

3. Economic Evaluation

It would be difficult to present the proposed recommendations in terms of exact economic justification. However, the impeller material change would result in less corrosion, less pump maintenance, and less downtime. Likewise, utilization of mechanical seals should also reduce maintenance and operating costs.

H. Mechanical Equipment Design

4. Recommendations

a. For all pumps it is recommended under all plant operating conditions, that the appropriate size and type mechanical seal be utilized in place of packing, and that the impeller material specified in the tables (and in accordance with Section IV-G of this report) be used.

b. For pumps in sea-water service special recommendations, based on previous discussion are: that P-3 be spared under any circumstances, and that P-5A be specified with a nine-foot can (three feet lower than present). The size of the latter will depend on the flow condition.

c. Special recommendations for the brine pumps, P-11 through P-22, are: that Monel 505 be specified for all impellers, and that with the recommended incorporation of mechanical seals, a flushing header containing product water be connected to each brine pump seal.

d. Condensate pump P-41 should be specified according to the pump table.

SECTION IV. GENERAL PLANT DESIGN

I. Instrumentation

1. Description of Plant Instrumentation

The instrumentation of the Freeport Conversion Plant is, in general, minimal. Many control functions are manual in nature. The condensate pumps are running with unthrottled discharge and are therefore subject to cavitation. The pH control is entirely manual and is subject to wide variation. However, the brine pumps are on level control. The vapor off the deaerator is controlled manually at approximately 40 per cent of the incoming stripping steam.

I. Instrumentation

2. Technical Evaluation

The condensate pumps are presently running with unthrottled discharge and insufficient net positive suction head to prevent flashing and cavitation. These pumps are capable of delivering 140 per cent of the required head with a resultant increase in capacity (approximately 150 per cent of design) at operating heads which allow the pumps to run dry and cavitate. This cavitation reduces the life of the impellers and does not enhance the process stability.

The pH of the sea water to the deaerator is now being controlled by manually setting the sulfuric acid injection metering pump stroke and watching the resultant pH record. Any changes in flow or pH of incoming sea water are reflected in the pH of the acidized sea water and the control operator must adjust the acid pump and water for pH change. Any adjustment must, therefore, be of a cut-and-try nature. The pH of the sea water to the deaerator ranges from 3.5 to 6.0 but usually averages 4.0 to 4.5.

Since the pH of the sea water to the deaerator is manually controlled and allowed to fluctuate, the pH of the deaerated sea water becomes harder to control. To further complicate the problem, this pH is also manually controlled by siphoning the sodium hydroxide solution into the suction line of the deaerator bottoms pump. Because of the susceptibility of glass pH electrodes to sodium ions, the pH record is not accurate and is used only as a trend record with random samples (lab analyzed) used as the correct pH for control settings.

The instrument air compressor is undersize for the present number of instrument air users, so the spare instrument air compressor must also run continuously in order to supply enough instrument air. During maintenance on either compressor, the construction air compressor must be used to make up the balance of the air requirements.

I. Instrumentation

3. Recommendations

A dollar savings value is difficult, if not impossible, to assign to the proposed instrumentation recommendations without extensive testing and evaluation. Only an approximate installation cost will be given with each recommendation.

a. The condensate pumps P-31 through P-42 should be placed on level control by installing a surge drum in the suction line after it leaves the flash chamber of the evaporator. All condensate pumped by the pump should first flow into the surge drum. The desired level is maintained by a displacement-type level controller which positions a butterfly valve in the condensate-pump discharge line. Thus, the flashing and cavitation are eliminated and the impeller life improved. This will cost approximately $650 per pump installed.

b. The pH of the sea water to the deaerator should be placed on automatic control by adding a controller and remote stroke adjusting mechanism to the acid pump. This would allow the pH control range to be narrowed, would free the control operator for other functions, and would make neutralization easier.

Glass pH electrodes are notoriously susceptible to poisoning by sodium ions, which makes neutralization with sodium hydroxide extremely difficult to control. However, if an antimony electrode is used, the susceptibility problem is eliminated. Additionally, the signal produced by this electrode is very large compared to a glass electrode. By the use of this type of electrode, a controller, and a control valve in the caustic siphon, better pH control may be obtained. Better pH control will produce better deaeration, will reduce corrosion and scaling in the system, and will save raw materials. The approximate installed cost would be $1050.

Dow currently holds a patent on one type of antimony electrode which it will make available to the Office of Saline Water Freeport Plant for evaluation. Other antimony electrodes are commercially available from firms such as Hartmann and Braun.

c. The instrument air compressor should have a capacity of approximately one standard cubic foot per minute per air user (e.g., transmitter or controller, or valve positioner) and the air receiver should be sized for a compressor four times the capacity of the compressor selected to allow the compressor to cycle. Instrument transmission tubing should be 3/8-inch outside diameter by 0.032-inch wall soft copper with a 0.032-inch extruded polyvinyl-chloride jacket. All joints and fittings should be taped with polyvinyl-chloride tape.

Compressor cost will vary depending on the number and type of compressors selected and the sparing requirements.

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

1. Review the data sample points and how chemical samples are handled; review the chemical analysis procedures. Make recommendations on analyses and sampling.

   a. Conclusions

      (1) Sample connections of 1/4-inch pipe size should be provided on the condensate lines of at least Effects I through IV. This is discussed in Section V-A-1-b.

      (2) In general, the procedures now being followed for both the handling of routine control samples and routine control analyses are applicable to the operating conditions and effective in obtaining the information needed for control. Suggestions are given in the discussion (Section V-A-1-b) regarding the handling of pH samples of deaerator feed brine, pH samples of product water, and alkalinity samples of product water.

      (3) The adoption of three additional methods of analysis is recommended for three periodic but non-routine samples taken at existing sample points. These are: a gravimetric CO_2 for deaerator effluent; a volumetric free CO_2 for product water; and a colorimetric (Indigo-Carmine) method for O_2 on deaerator effluent when required. These are discussed below.

   b. Discussion

      The installation of sample connections in the condensate (product water) lines from Effects II through VI, would be justified during a study of the residual CO_2 distribution between brine and product water at various brine pH values of deaerator effluent. Such a study is best based directly on the analyses of sets of synoptic samples, rather than on calculations from mass-transfer kinetics.

      The pH of the feed brine to the deaerator, as it exists inside the feed line, has a value which differs from the pH value of a sample of the feed brine allowed to cool to room temperature and to come to equilibrium with normal air. The size of the difference depends upon the initial pH value. If the pH of the brine inside the deaerator feed line is actually 3.8 or less, then most of the average 90 parts per million gross CO_2 content will exist in the brine as free CO_2 (refer to Figure IV-C-6). When a sample of brine at this actual pH value is withdrawn from the line and exposed to normal air, it will cool, and also some of the CO_2 will escape to the atmosphere. Since nearly all the CO_2 of the sample is present as free CO_2, no further pH change can take place, and the pH of the sample will be the same as that of the brine, from a practical standpoint. If the pH of brine in the feed line is actually, say 4.2, then there will be appreciably more HCO_3^- ion present. When the sample is exposed to air, and the CO_2 escapes, a shift in equilibrium occurs which is summarized by:

$$HCO_3^- \rightarrow CO_2 + OH^-,$$

or a shift to the right in the following equilibrium:

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

The OH^- ion liberated is sufficient to increase the pH to 5.0. This relationship is shown in Figure V-A1-1.

Since P_{CO_2} in a sample is about 0.1 atmosphere at low pH values, precautions necessary to accurately measure the initial pH will make the procedure inconvenient. The following procedure is therefore suggested:

> If the sample produces a reading of 4.0 or less on the pH meter, record the reading. If the sample produces a reading of greater than 4.0 on the pH meter, withdraw the sample from the meter, and pour it repetitively back and forth between beakers for a standardized number of times, and redetermine the pH with the pH meter. Record the reading. Identify the record column as "pH in air".

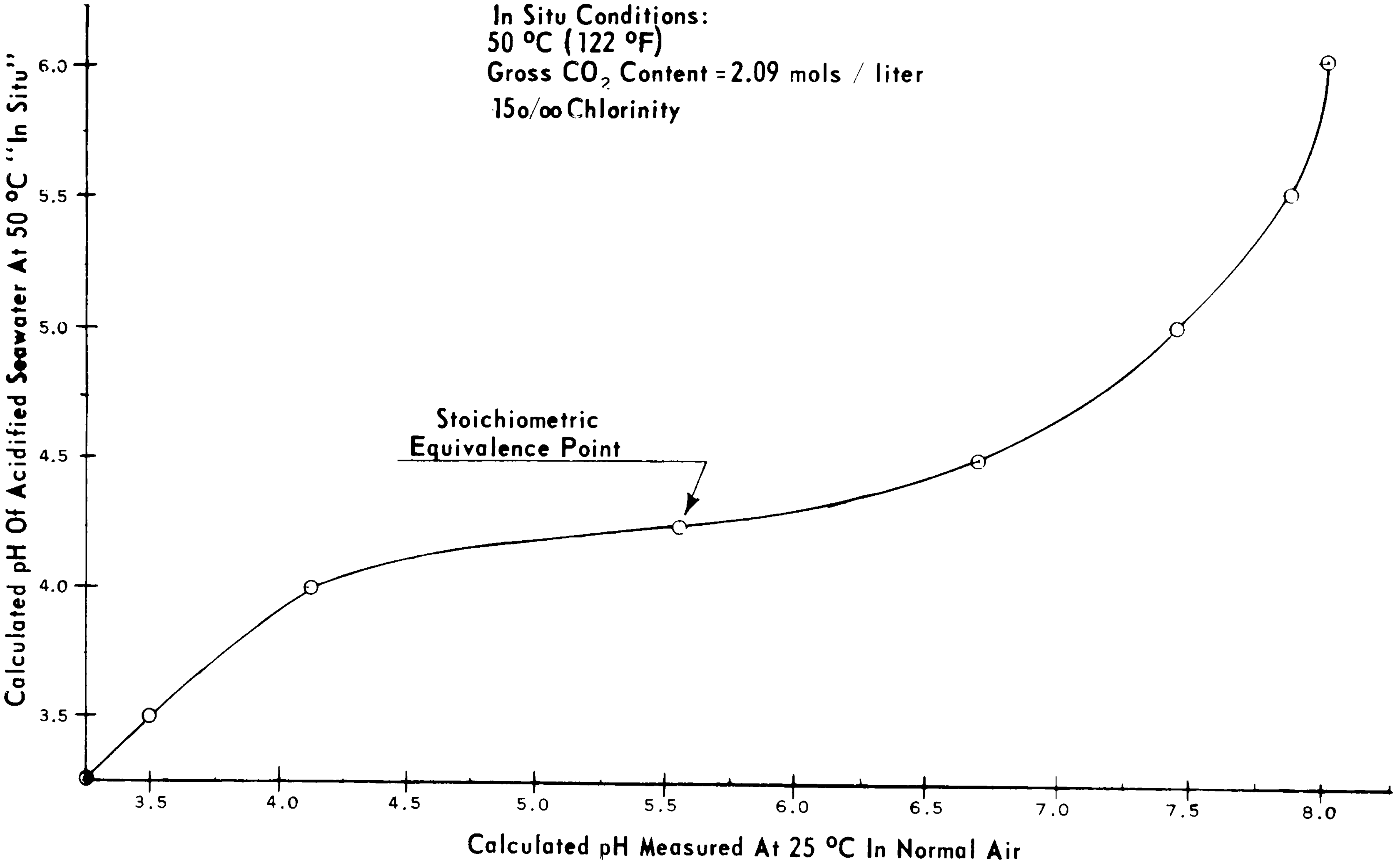
The routine pH determination of samples of product water can create a problem similar to the one just described, if the product water contains free CO_2, or, to a lesser degree, if it contains an appreciable excess of Na_2CO_3. In the first case, with free CO_2 present, the pH in the line will be lower than that after the sample comes to equilibrium with air. Relationships exist here, similar to the one shown in Figure V-A-1, but with the flat portion of the curve in a different pH range. Since the amount of free CO_2, or of excess $CO_3^=$, will vary, the actual pH value in the line is relatively less meaningful here than with the deaerator. What is important is whether the pH value increases or decreases when the sample is exposed to air and the magnitude of the change. The following procedure is recommended on the routine pH samples obtained from the product water line to Freeport:

> Obtain the sample in the same container in which the electrode of the pH meter is inserted, and which is provided with a large rubber stopper. Allow the water sample to fill the container completely to minimize contact with air while sample is being carried. Remove stopper and measure initial pH of sample. Remove sample from pH meter. Pour sample repetitively between two beakers a set number of times, as previously described, to allow the sample to come to equilibrium with air. Redetermine pH value with pH meter. Record both values.

If the pH in air is appreciably greater than the initial pH, as determined by experience, then the free CO_2 should be determined later, as a non-routine determination, as described in one of the following paragraphs.

Total dissolved O_2 is now being determined on non-routine samples of the caustic-treated deaerator effluent by the Winkler method. The latter should be sensitive to as low as 0.01 part per million, although many authorities claim 0.05 part per million is as low a value as can be consistently reproduced. A suggested method for complementing the Winkler method, is the Indigo-Carmine method(12), which is applicable only between 0.001 and 0.150 part per million dissolved O_2. It is a colorimetric method and has proved itself reliable in industry.

FIG. V - A - 1
"IN SITU" pH vs pH MEASURED AT 25 °C IN NORMAL AIR



In Situ Conditions:
50 °C (122 °F)
Gross CO_2 Content = 2.09 mols / liter
15o/oo Chlorinity

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

The following considerations are offered regarding the alkalinity titration of the sample of caustic-treated deaerator effluent. First, what is really wanted here is a determination of the total CO_2 content for a check on deaerator performance, and not necessarily carbonate-bicarbonate alkalinity. Second, if the deaerator is not functioning properly, considerable dissolved CO_2 may be present at a pH of 6.8, which may escape determination unless the sampling technique includes "fixing" the CO_2 with caustic in the closed sampling container. Third, if the deaerator effluent actually contains, say, 1.0 part per million total CO_2 at a pH of 6.8, it is possible to absorb CO_2 from the atmosphere, either during sample handling or during titration. This amount of absorbed CO_2 could be as high as three times the initial CO_2 content unless adequate precautions are taken. (From Figures IV-C-2 and IV-C-6, the total CO_2 concentration in brine at 25°C, and at pH 6.8 in equilibrium with normal air, is 3.7 parts per million.)

If the total CO_2 in the deaerator effluent were determined gravimetrically using an absorption train, precautions would still be necessary with sample handling, and with moisture films on the outside of the U-tube. It is felt that the advantages of the gravimetric method outweigh those of the volumetric method, and is being recommended here as a periodic non-routine check on deaerator performance.

If routine control samples indicate the presence of free CO_2 in the product water, then the free CO_2 should be determined by the carbonate titration method(10) on a non-routine sample.

Ascribing the "alkalinity" of the deaerator effluent entirely to the presence of bicarbonates (plus free CO_2) in the sample, which is apparently the present practice, leads to conclusions which are considerably in error. The bicarbonate content inferred from this practice could be many times greater than actually exists. The analytical procedure, presently prescribed for the Freeport Conversion Plant for the determination of carbonates and bicarbonates, mentions the fact that the method assumes the absence of the salts of weak acids, such as boric. It does not state how to correct for the presence of borates, which are always present in sea water.

As an example of what is meant in the above paragraph, consider a deaerator effluent brine of chlorinity = 19 parts per thousand, having, in fact, a residual total CO_2 concentration of 2.0 parts per million CO_2 (= 2 x 50/44 = 2.26 parts per million $CaCO_3$ "alkalinity").

Assuming that the end-point error is equal to +2.0 parts per million $CaCO_3$, the result reported for this sample would be an "alkalinity" of 4.46 parts per million $CaCO_3$, *if no borates were present*. As a matter of fact, sea water of 19 parts per thousand chlorinity contains about 4.5 parts per million boron. This is equivalent to: 4.5 x 50/10.8 = 20.8 parts per million $CaCO_3$. About one-third of this amount of boron (actually, 6.5 parts per million of $CaCO_3$ equivalent) will be titrated if the sample, as presently prescribed in the analytical procedure is first adjusted to the phenolphthalein end-point prior to titration to the methyl-orange end-point. The result reported for the alkalinity determination would now be: 2.26 + 6.5 + 2.0 = 10.76 parts per million $CaCO_3$, which can erroneously be interpreted to be due entirely to bicarbonates. This amounts to 475 per cent of the alkalinity equivalent to the bicarbonate concentration.

In order for the "alkalinity" of the deaerator samples to be a measure of the residual CO_2, the alkalinities now being reported as a result of the titration procedure now in effect should be corrected for the amount of borates present by subtracting the following quantities. These corrections(19) are valid only if the sample is adjusted to a pH of 8.3 at 30°C prior to titrating to the methyl-orange end-point:

Chlorinity of Sea Water %	Value to be subtracted from "Methyl-Orange" Alkalinity to Correct for Borates ppm $CaCO_3$
15	4.5
17	5.5
19	6.5
21	7.5

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

As a practical matter, as well as a point of theoretical chemistry, it would be advantageous to speak in terms of total CO_2 existing in the deaerator effluent and not in terms of "alkalinity".

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

2. Review the acid and caustic treatment of sea-water feed, based on existing data of acid demand and alkalinity residual. Make recommendations on treatment design.

   a. Conclusions

      (1) The average rate of sulfuric-acid addition to the deaerator feed (50 pounds of 94 per cent H_2SO_4 per hour based on operating records for the period of this study) is not quite sufficient to continuously maintain the deaerator effluent at pH four, the value required for good decarbonation. This fact, together with the hourly fluctuations in pH of the deaerator feed, means that for a considerable portion of operating time the pH of the feed is higher than even the present control point of 4.5 pH.

      (2) Manually controlling the sulfuric-acid addition to the deaerator feed brine (the present method) is unsatisfactory. It has resulted in excessive variation in pH, poor deaerator efficiency, and could lead to excessive acid consumption. These objections are inherent in the method of control and do not imply poor operation under the existing conditions.

      (3) The rate of caustic addition to the deaerator effluent (25 gallons per day of 50 per cent NaOH, as quoted by the Freeport plant operating personnel) agrees reasonably well with the observed average pH (six to eight) of the effluent and the residual CO_2 content (six parts per million) of the deaerator effluent. This rate of caustic addition, 25 gallons per day of 50 per cent NaOH, does not agree with the 0.031 pounds of 50 per cent NaOH per thousand pounds of sea water fed given in "Development Report No. 1" by Stearns-Roger(49).

      (4) Manually controlling the rate of caustic addition to the deaerator effluent is unsatisfactory. It has resulted in wide deviations of the pH of the deaerator effluent from the desired control point

value, and may result in excessive caustic consumption.

(5) The points mentioned are discussed in Section V-A-3.

b. Recommended Revisions for Acid - Caustic Treatment

(1) Install automatic control equipment for acid addition to deaerator feed. The sensitive element should be an antimony pH electrode and the acid feed pump should be of the rapid-stroke type, either double-acting or two-cylinder.

(2) Relocate point of acid addition to the deaerator feed line farther upstream from the spray nozzle. The new location should allow appreciably more pipeline distance between the injection point and the deaerator spray nozzle than exists at present. The new distance should be at least fifteen feet. When installed, the sample tap for the pH control should be as close as possible to the spray nozzle.

(3) Maintain the pH of the deaerator feed at a value not to exceed 4.0 pH, say between 3.8 and 4.0. This is critical to the deaerator operation and should be done immediately.

(4) The bases for the above recommendations are discussed in Section V-A-3.

c. Discussion

As stated already in a previous section of this report, if the pH of the deaerator effluent were maintained at a higher value than at present, the corrosive conditions of both the brine system and the product-water system would be considerably reduced. The following considerations indicate that a higher pH than the existing 6.8 control value for the deaerator effluent can be maintained without undue risk of $CaCO_3$-$Mg(OH)_2$ scale formation.

Assumptions are made that the residual CO_2 concentration of the deaerator effluent is 8.0 parts per million CO_2, (= 9.1 parts per million $CaCO_3$ alkalinity) and that the concentration of dissolved solids in the brine in the localized areas of supersaturation(33) will not exceed three times the concentration of dissolved solids in the body of the liquid. At a concentration factor of 1.0, the concentration of Ca in the brine = 410 parts per million = 1020 parts per million $CaCO_3$. In the localized supersaturated areas of the initial effects this will be 3060 parts per million $CaCO_3$. Langelier's diagram for 100°C(32) indicates no carbonate scale would form below a pH of 7.8 under these conditions. In the localized supersaturated areas, the concentration of Mg would be:

3 x 1300 = 3900 ppm Mg = 15,600 ppm $CaCO_3$.

The same Langelier's diagram indicates no $Mg(OH)_2$ scale would form at 100°C under these conditions below a pH of 7.7.

At a concentration factor of 3.0, corresponding to the concentration in Effect XII, the Ca concentration in the areas of supersaturation would be:

3 x 3 x 410 = 3690 ppm Ca = 9250 ppm $CaCO_3$.

From the Langelier's diagram for 50°C(31), no carbonate scale will form under these conditions below a pH of 7.7. Also, under these conditions the concentration of Mg in the areas of supersaturation would be:

3 x 3 x 1300 = 11,700 ppm Mg = 48,000 ppm $CaCO_3$.

The Langelier's diagram for magnesium-hydroxide stability(30) indicates no $Mg(OH)_2$ scale would form under these conditions below a pH of 7.8.

The foregoing indicates that theoretically no carbonate-hydroxide scale would be formed from brine whose pH was below 7.7, at temperatures up to 100°C, and under the conditions of the two initial assumptions. A pH control point of 7.3 on the brine effluent from the deaerator would be a practical value for operation. Automatic control of the caustic addition would insure a minimum of deviation from the control point. The use of the ion-exchange step for softening the sea water would enable the brine to be maintained at much higher pH values.

Of the two initial assumptions made, the first should be very safe. A residual CO_2 concentration in the deaerator effluent of eight parts per million should be easily maintained. The validity of the second assumption is more difficult to determine. Information obtained from the literature is conflicting in the statements concerning the degree of "over-concentration" existing in the areas of localized supersaturation.

d. Suggestion for Further Research

In view of the final statement of the preceding paragraph, there is a need for empirical, experimentally obtained information indicating the pH value at which carbonate-hydrate scale is first detected in a falling-film evaporator tube at temperatures up to 120°C and at concentration factors up to about five.

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

3. Review the deaerator operation from data now available. Determine the kinetics of chemical neutralization and the mass-transfer rates for gas removal. Review the methods of control including the present use of sulfite. Determine the effects of temperature on the deaerator.

a. Deaerator Operation

The deaerator operation on April 10, 1964, with respect to O_2 and CO_2 removal is shown on Figures IV-C-8 and IV-C-9. The pH of the feed brine was deliberately adjusted to a value of 3.9 to 4.0 for the duration of the run, from the then normal control point of 4.5. The gross CO_2 in the leaving brine was determined gravimetrically on duplicate samples. This value, 2.8 parts per million, is lower than the corresponding values obtained with operation at a higher feed brine pH.

On June 10, 1964, all the packing was removed. Several sets of samples were taken with the deaerator operating without packing and with the inlet pH at 4.0 or below. The effluent showed between 0.01 and 0.10 part per million O_2, and a gross CO_2 content of about eight parts per million as determined by gravimetric analyses.

(1) The conclusions arrived at in this study are:

(a) The deaerator will perform as a decarbonator up to the limitations imposed by the inherently unfavorable liquid:vapor rate if the pH of the feed brine is 4.0 or less.

(b) Because of the high liquid:vapor rate there is little promise that the CO_2 content of the effluent can be reduced much lower than two parts per million, unless the steam flow from Effect XI is increased considerably.

(c) Increasing the rate of stripping steam from Effect XI will lower the residual CO_2 slightly, by moving internal conditions toward a true countercurrent situation.

(d) Conclusions similar to (b) and (c) are valid also for O_2, i.e., its concentration of 0.01 part per million in the effluent, already satisfactory, could be reduced still further if countercurrent conditions could be attained.

(e) Increasing the rate of leaving vapor will also decrease the residual O_2 and CO_2 concentrations in the deaerator effluent.

(2) Recommendations for continued deaerator operation are:

(a) With pH maintained at 3.8 to 4.0, and with leaving vapor rate held constant, plot CO_2 residual against rate of stripping steam from Effect XI as was done by Stearns-Roger(49), to determine lowest practical steam rate, and lowest obtainable CO_2 residual. This should be done over a period of days, with no other changes made simultaneously.

(b) Determine quantitative effect of leaving vapor rate on CO_2 residual at fixed steam rates, with entering pH maintained at 3.8 to 4.0.

(c) Avoid changing two variables simultaneously.

b. Determine the kinetics of chemical neutralization and mass-transfer rates for gas removal.

(1) Conclusions

(a) There is insufficient opportunity for complete mixing and neutralization of the deaerator feed brine and sulfuric acid to occur in the existing plant between the point of acid injection and the point of sampling (directly above the spray nozzle). This conclusion is based on empirical industrial experience.

(b) The over-all mass-transfer coefficients for the desorption of O_2 and CO_2 from sea water at 122°F as used in this study are:

For O_2: K_La = 260 lb-mol/hr/cu ft per lb-mol/cu ft
= 1.63×10^{-2} lbs O_2/hr/cu ft per ppm concentration difference
= 0.43 lbs O_2/hr/cu ft per atm partial pressure difference

For CO_2: K_La = 200 lb-mol/hr/cu ft per lb-mol/cu ft
= 1.27×10^{-2} lbs CO_2/hr/cu ft per ppm concentration difference
= 9.63 lbs CO_2/hr/cu ft per atm partial pressure difference

The above values were extrapolated from literature values (see Table IV-C-II) for sorption of O_2 and CO_2 from fresh water, using air.

(2) Discussion

In order to efficiently strip sea water of its total CO_2 content on an industrial scale, the carbonate and bicarbonate ions present in the normal pH range of 8.0 to 8.3, (Figure IV-C-6) must first be converted to free CO_2. From a practical standpoint this condition exists at 4.0 pH. Of the four species of the CO_2 system existing in sea water, only free CO_2 exerts a vapor pressure, the driving force in the desorption process.

The neutralization process involves adding the acid to the sea water, inducing dispersion of the acid in the sea water, neutralization of HCO_3^- by the acid, and measurement of the pH for control, all before the mixture is sprayed into the desorber. Of these processes, it is the proper design of a mixing system to insure dispersion of the acid in the brine before its pH is measured, that is the difficult problem. Industrial experience indicates that the present four feet of eight-inch pipe containing two orifices is an inadequate mixing device between acid injection point and sampling point. The optimum design would require experimentally obtained data.

The neutralization of the HCO_3^-, i.e., conversion of the latter to free CO_2 can proceed by either:

$$HCO_3^- \longrightarrow CO_2 + OH^- \qquad (1)$$

or by:

$$\begin{aligned} HCO_3^- + H^+ &\longrightarrow H_2CO_3 \qquad (2) \\ H_2CO_3 &\longrightarrow CO_2 + H_2O \qquad (3) \end{aligned}$$

It is known that the reaction rate of (2) is very much greater than either (1) or (3). Therefore, the reaction time required for a certain concentration of HCO_3^- to be essentially completely converted to dissolved CO_2 will never be greater than that required by the faster of the two reactions, (1) or (3). Brinkman, et al.(11) experimentally determined values for the reaction rate constant for reaction (3), which vary between $k = 1.7$ and $k = 9.5$ reciprocal seconds at 15°C, depending on pH range. This indicates a time of about one second for 99 per cent complete reaction at 15°C. Their value for the increase in reaction rate constant with temperature, $Q_{10} = 2.9$, gives a value of about 0.025 seconds as the time required for essentially complete reaction at 50°C via reaction (2) and (3), above. This means that the maximum time required at 50°C for the neutralization process alone to attain essential completion, assuming initial instantaneous mixing, is a relatively small factor compared to the difficulty of mixing viscous, concentrated H_2SO_4 with sea water.

The dissolved free CO_2 must now be released from solution. All processes for effecting the release of dissolved gases depend upon contacting the liquid with a gas phase in which the partial pressure of the solute gas is less than the equilibrium pressure at the concentration of the solute in the liquid. At a given temperature, the rate of transfer will be proportional to the area of contact surface between liquid and gas phase, and proportional to the difference between the equilibrium pressure of the solute gas in the liquid and its partial pressure in the gas phase. The majority of the surface area required is furnished by the tower packing. A considerable amount of contact area is also afforded by droplet surface area, by wetted walls, and by steam bubbles, if any.

The partial pressure of CO_2 in the gas phase, the stripping steam from Effect XI in this case, must be less than the equilibrium pressure of the CO_2 (P_{CO_2}) in the brine. To insure as great a driving force as possible, P_{CO_2} should be as great as possible. This is the reason for neutralizing to a pH of 4.0 instead of stopping at a higher value, say at 5.6 pH, the stoichiometric equivalence point. This is not a question of whether sea water can be decarbonated at higher pH values. It is an attempt to obtain as high a driving force as possible in a stripping column in which it is fairly certain that countercurrent conditions are lacking. Langelier succeeded in completely decarbonating a sample of unacidified sea water in 333 minutes by boiling under carefully controlled conditions(34).

Although maintaining, say 3.9 pH in the deaerator effluent does consume more sulfuric acid than neutralizing to 5.6 pH, the small additional cost is considerably less than the cost of the troubles caused by residual CO_2 in the deaerator effluent. The additional cost of chemicals to neutralize to pH = 3.9 instead of to 5.6 per million pounds of sea water fed is:

Cost of H_2SO_4 to 5.6 pH = $1.18
Cost of H_2SO_4 to 3.9 pH = $1.24
Cost of NaOH, 5.6 to 7.0 pH = $0.01
Cost of NaOH, 3.9 to 7.0 pH = $0.34
Total cost difference = $0.39

The costs listed above, if converted to the basis of cents per one thousand gallons of product water at the present (April, 1964) operating conditions of the Freeport Conversion Plant are:

Cost of H_2SO_4 to 5.6 pH = 1.32
Cost of H_2SO_4 to 3.9 pH = 1.39
Cost of NaOH, 5.6 to 7.0 pH = 0.01
Cost of NaOH, 3.9 to 7.0 pH = 0.38
Total cost difference = 0.44

The above estimate assumes sulfuric acid and caustic soda at their current delivered cost at Freeport, and assumes 105 parts per million CO_2 in the deaerator feed.

In order for countercurrent action to obtain in the deaerator, and in order for the calculation of packing requirement to be valid, the upward flow of stripping steam at any point in the packing must approximate the leaving vapor rate. If no stripping steam were admitted to the deaerator below the packing, then the leaving vapor rate would be constituted almost entirely by vapors "flashing" from the brine in the upper portion of the tower. Increasing the leaving vapor rate by lowering the pressure in the exit line, or by increasing the brine temperature would merely increase the amount of "flashing" occurring in the upper layers of packing. Admitting vapors from Effect XI into the deaerator is necessary for good deaerator performance.

c. Methods of O_2 Control

Practical methods of O_2 control in steam and water systems are either mechanical or chemical. The former category includes insuring tight joints between all pairs of mating surfaces on systems operating under vacuum, and the venting of bleed streams from points where non-condensables accumulate. Chemical treatment consists of injecting either sodium sulfite or hydrazine, or both, into the liquid phase. Both of these are reducing agents upon which the dissolved O_2 spends itself.

The lowest cost and most rewarding method of maintaining an initially low O_2 content in the desired range is insuring of tight seals at gasketted joints and the use of properly designed seals and wearing rings at the stuffing boxes of centrifugal pumps. There is ample opportunity for O_2 leakage from the atmosphere at the Freeport Conversion Plant at any of the points mentioned above located downstream from Effect III.

Venting the bleed stream of non-condensables, cascade fashion, from heating element to heating element eliminates O_2 from the system at the cost of downgrading the recoverable heat in the steam of the bleed stream. Regarding the disposition of the vent stream from Effects II and III, the conclusion here is that it continue to be vented downstream instead of being fed to the deaerator.

An estimate of the total number of inches of periphery of gasketted joints existing on the various effects plus their accessories, indicates approximately 800 linear inches per effect. An approximate practical value has been given(15) for the amount of air inleakage which reasonably might be expected to occur through an average gasketted joint of a vacuum system. This is 0.2 pounds O_2 per hour per 1000 linear inches of periphery. Using this value, the total amount of O_2 inleakage which might be expected, then, from Effect IV through Effect XII would be 1.54 pounds O_2 per hour.

As a chemical method of O_2 control, sodium sulfite (Na_2SO_3) is added to boiler water systems. Under the prevailing conditions, the Na_2SO_3 is a reducing agent, and reduces dissolved O_2 according to the over-all reaction:

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$$

Whether the above reaction proceeds directly as shown above or whether the mechanism is through some intermediate compound formation is of some practical significance, since a short reaction time is very desirable. In order to increase reaction rate, industrial practice(9) is to add a proprietary mixture of Na_2SO_3 and a catalyst of cobalt or manganese salts which are apparently very effective in reducing the reaction time from the order of minutes to seconds.

Theoretically, it requires approximately 7.9 pounds of Na_2SO_3 to reduce 1.0 pound of dissolved O_2. Thus, if the residual O_2 content in the deaerator effluent were, say 0.1 part per million, it would require the feeding of $0.1 \times 10^{-6} \times 490{,}000 \times 7.9 = 0.39$ pounds of Na_2SO_3 per hour to the brine to reduce the dissolved O_2 to a theoretical zero part per million.

A question has been raised concerning the solubility of $CaSO_3$ in sea water. The point in question is whether the $SO_3^=$ ion added will cause $CaSO_3$ to precipitate from solution on heating surfaces to form a $CaSO_3$ scale, and whether the latter would offer convenient sites to initiate the formation of $CaSO_4$ scales under conditions of supersaturation. There is insufficient solubility data in the literature to answer this question with confidence. It involves also a knowledge of reaction kinetics, i.e., rate of oxidation of $SO_3^=$ ion versus rate of precipitation of $CaSO_3$. What information is known about $CaSO_3$ is translated to as useful a form as possible in the following paragraphs.

Van der Linden(42) gives the following data on the solubility limit of $CaSO_3$ in fresh water:

Temperature, °C	Gms $CaSO_3 \cdot 2H_2O$ per Kg
30	0.064
40	0.063
50	0.057
60	0.061
70	0.045
80	0.031
90	0.027
100	0.011

From the above values, the pseudo-solubility product (k) for $CaSO_3$ in fresh water can be calculated at 50°C and 100°C. These are:

At 50°C: $k = 430\ (ppm)^2$
At 100°C: $k = 15.8\ (ppm)^2$

The solubility product of $CaSO_3$ will be greater in sea water than in fresh water due to total ionic-strength effects. The approximate magnitude of the effect will be the same for $CaSO_3$ as for $CaSO_4$. By using the known ratio of the solubility of $CaSO_4$ in 15 parts per thousand chlorinity sea water(28) to that in fresh water(43), the above values become:

At 50°C: $k = 1160\ (ppm)^2$
At 100°C: $k = 45.5\ (ppm)^2$

indicating that the limit of solubility of $CaSO_3$ in 15 parts per thousand chlorinity brine is: 3.75 parts per million $CaSO_3$ at 50°C, and 0.145 part per million $CaSO_3$ at 100°C.

Using the above values, the following conclusions can be drawn regarding the use of Na_2SO_3 at the Freeport Conversion Plant:

(1) Injection of Na_2SO_3 into the deaerator effluent will probably not result in $CaSO_3$ scaling if the rate of addition at the

deaerator does not exceed 3.5 parts per million (based on sea-water feed) and if the residual Na_2SO_3 measured at heat exchanger 304 does not exceed 0.1 part per million in concentration.

(2) Use only Na_2SO_3 in proprietary mixtures which also contain a catalyst to increase the reaction rate. This will minimize the chance for unreacted Na_2SO_3 to reach a temperature zone where the limit of its solubility is exceeded.

(3) The use of an ion-exchange softening process to reduce the calcium content of the brine will make the use of Na_2SO_3 much more attractive as an O_2 scavenger. The solubility limit of $CaSO_3$ will be increased many fold.

Sodium sulfite can also act as an oxidizing agent. Therefore, it is possible to form H_2S and elemental sulfur in boiler systems, and in the Freeport Conversion Plant by the use of Na_2SO_3. This would form as a product of reaction of the Na_2SO_3 on organic materials present in the sea water. This is not a very probable occurrence at concentrations of residual Na_2SO_3 no greater than 0.1 part per million.

Hydrazine (N_2H_4) is also used in commercial boiler water systems to scavenge dissolved O_2. It is a much more powerful reducing agent than Na_2SO_3. Latimer(26) gives the standard oxidation potential (E_B^0) as + 1.6 volts at 25°C for the following reaction:

$$4\ OH^- + N_2H_4 = N_2 + 4\ H_2O + 4\ e^-$$

Its higher unit cost, about $1.30 per pound, is partially offset by its lower molecular weight, resulting in a requirement of only 1.0 pound per pound of O_2 scavenged, compared with 7.9 for Na_2SO_3. It is used to advantage in high pressure systems requiring low total dissolved solids, since it does not increase the solids content.

Hydrazine is both toxic and flammable. Another large disadvantage is that it can undergo auto oxidation-reduction:

$$2\ N_2H_4 \longrightarrow 2\ NH_3 + N_2,$$

resulting in concentrations of ammonia in the system. At high enough levels, the ammonia can attack copper or zinc alloys at an appreciable rate. The ammonia can also be carried over to the condensate where it could attack the brass mountings of valves.

The use of hydrazine as an O_2 scavenger is not recommended in the Freeport Conversion Plant.

An instrument that would be invaluable in O_2 control at the Freeport Conversion Plant is the "OXYMETER" (manufactured by Magna Corporation, Santa Fe Springs, California). This is a portable direct reading meter with an O_2-sensitive element located in a probe at the end of a flexible cord. This instrument would greatly facilitate O_2 determinations of the deaerator effluent. It is sensitive to one part per billion dissolved O_2. Its basic price is approximately $200.

d. Effects of Temperature on Deaerator

Under the following invariant conditions:

(1) Leaving vapor rate = 1050 pounds per hour,
(2) Entering brine rate = 490,000 pounds per hour,
(3) Rate of stripping-steam injection below packing = 900 to 1500 pounds per hour,
(4) Countercurrent action inside packing approached to same extent as at present,
(5) Concentrations of O_2 and CO_2 in entering brine remain at present values,

the effect of a major temperature increase on the present deaerator would either be a reduction in packing requirement, for the same concentrations of O_2 and CO_2 in the leaving brine, or, an undetectable lowering of the concentrations of O_2 and CO_2 in the leaving brine, if the packed height were allowed to remain unchanged.

Table V-A-3-I shows quantitatively the new packing requirement for the present deaerator resulting from a theoretical change in the temperature of the feed brine from the present value of 122°F to 232°F, with the concentrations of O_2 and CO_2 in the feed brine remaining the same. The new operating total pressure inside the deaerator will be slightly below the saturation pressure for 232°F in order to hold the leaving vapor rate unchanged. The steam introduced below the packing under the new conditions would have to be vapors from Effect I.

Of the five conditions listed in the first paragraph, it is the fourth condition (countercurrent action) to which outlet concentrations of CO_2 and O_2 will be the most sensitive in the present deaerator operating under existing conditions. Any change which will improve the approach to countercurrent action will lower the outlet concentrations of O_2 and CO_2; for example, increasing the flow of inlet steam below the packing. The general objective of steam rate adjustments is to cause as high a percentage as possible of the vapors originating below the packing, to appear in the outlet vapor stream. Thus, the pressure drop across the packing should be maintained at as high a value as possible, consistent with the heat economy implications of introducing a high rate of steam below the packing.

Referring to Table V-A-3-I, the capital savings resulting from operating the deaerator at 232°F would not be as great as the tabulation might imply. Although there would be a savings in packing, along with a corresponding savings in tower height, the required diameter of the tower would remain at six feet.

In the general case, the expression for the packing requirement of a stripping column desorbing a given quantity of solute between fixed terminal concentrations, is:

$$V = \frac{Q}{K_L a \times \text{log mean } \Delta P},$$

where:

V = volume of packing in cubic feet,
Q = pounds of solute gas desorbed per hour,

K_La = over-all liquid-film mass-transfer coefficient, expressed here as pounds per hour per cubic foot per atmosphere difference in partial pressure,

ΔP = differences between equilibrium pressure of solute and partial pressure of solute in the gas phase at the terminal conditions.

In the specific case of the existing deaerator, the operating line is relatively far from the equilibrium line (Figure IV-C-9). The partial pressure of CO_2 in the gas phase is therefore insignificant in its effect on the value of log-mean ΔP. A change in total operating pressure, necessitated by a temperature change, would therefore have a negligible effect on the value of log-mean ΔP, and the packing volume would vary inversely as the product of K_La and P_{CO_2}. This situation is reflected in the values listed in Table V-A-3-I. The effect of a temperature change from 50°C to 111°C is a sixfold reduction in packing requirement.

If the deaerator were operating under the initial conditions shown in Table V-A-3-II, the operating line would be fairly close to the equilibrium line. The partial pressures of CO_2 in the gas phase are close to the values of P_{CO_2} in the liquid, and therefore cannot be neglected. A temperature change to 111°C would demand the same increase in total operating pressure as before. In this case, however, the new operating pressure has caused a ninefold decrease in log-mean ΔP resulting in a packing requirement that is three times the former value.

TABLE V-A-3-I

DEMONSTRATION OF EFFECT OF TEMPERATURE ON DEAERATOR OPERATION

CASE I: (Design Conditions for Existing Deaerator at 50°C)

Brine Rate = 490,000 lbs/hr
Leaving Vapor Rate = 1,050 lbs/hr
CO_2 in Entering Brine = 105 ppm
CO_2 in Leaving Brine = 0.5 ppm

	50°C = 122°F	111°C = 232°F
P_{CO_2} of Entering Brine, atm	1.39×10^{-1}	3.07×10^{-1}
P_{CO_2} of Leaving Brine, atm	6.6×10^{-4}	1.45×10^{-3}
Mol Fraction CO_2 in Entering Vapor	2.04×10^{-7}	2.04×10^{-7}
Mol Fraction CO_2 in Leaving Vapor	2.01×10^{-2}	2.01×10^{-2}
Total Pressure Inside Deaerator, atm	0.102	1.44
Partial Pressure CO_2 in Entering Vapor, atm	2.08×10^{-8}	2.94×10^{-7}
Partial Pressure CO_2 in Leaving Vapor, atm	2.05×10^{-3}	2.89×10^{-2}
K_La, lbs/hr/cu ft/atm	9.63	28.0
Volume Packing Required, cu ft	207	34.9

NOTE: Ratio of packing requirements to be compared with that shown on Table V-A-3-II.

TABLE V-A-3-II

DEMONSTRATION OF EFFECT OF TEMPERATURE ON DEAERATOR OPERATION

CASE II: (Hypothetical Conditions)

Brine Rate = 490,000 lbs/hr
Leaving Vapor Rate = 130 lbs/hr
CO_2 in Entering Brine = 50 ppm
CO_2 in Leaving Brine = 0.05 ppm

	50°C = 122°F	111°C = 232°F
P_{CO_2} of Entering Brine, atm	6.63×10^{-2}	1.47×10^{-1}
P_{CO_2} of Leaving Brine, atm	6.63×10^{-5}	1.47×10^{-4}
Mol Fraction CO_2 in Entering Vapor	2.04×10^{-7}	2.04×10^{-7}
Mol Fraction CO_2 in Leaving Vapor	1.0×10^{-1}	1.0×10^{-1}
Total Pressure Inside Deaerator, atm	0.102	1.44
Partial Pressure CO_2 in Entering Vapor, atm	2.08×10^{-8}	2.94×10^{-7}
Partial Pressure CO_2 in Leaving Vapor, atm	1.02×10^{-2}	1.44×10^{-1}
K_La, lbs/hr/cu ft/atm	9.63	28.0
Volume Packing Required, cu ft	308	923

NOTE: Ratio of packing requirements to be compared with that shown on Table V-A-3-I.

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

4. Evaporator Scaling

a. Solubilities of Calcium Sulfate and Its Hydrates

The nature of the evaporative processes in the long-tube, vertical, falling-film, distillation system makes an accurate knowledge of the solubilities of the scale-forming compounds imperative. The thin films on the tube walls, the turbulence associated with the vapor formation, and the concurrent vapor liquid flow all act to reduce to a minimum the allowable supersaturation of any scale forming compounds.

The proper addition of acid to neutralize the alkalinity in the feed sea water followed by proper degassing will prevent formation of the alkaline scales, calcium carbonate and magnesium hydroxide.

Calcium sulfate, in its various hydrated forms, is the most troublesome scale encountered in the distillation of sea water. It is known that anhydrous calcium sulfate occurs as scale at high temperatures and that the dihydrate (gypsum) occurs as scale at low temperatures. Both forms, as well as the metastable hemihydrate, have been found as major constituents of scale samples taken from the tube walls in the Freeport Conversion Plant.

A study was undertaken to determine, using available references, the best solubility relationships for these forms of calcium sulfate in concentrated sea waters at elevated temperatures.

The most complete information on the solubilities of calcium sulfate was found in a paper by W. L. Marshall, Ruth Slusher and Ernest V. Jones(28).

The solubility of $CaSO_4 \cdot 2H_2O$ (gypsum) was determined by Marshall at 40 and 60°C and $CaSO_4$ (anhydrite) at 125, 150, 175, and 200°C in $NaCl-H_2O$ solutions varying from zero to four molal NaCl. These data, combined with additional literature values, agreed with Debye-Hückel theory at all temperatures and over the range of concentrations when a function of ionic strength was used in the correlation. Marshall and associates concluded that from the solubility results, in agreement with Debye-Hückel theory, it should be possible to estimate the solubilities of $CaSO_4$ and its hydrates at temperatures between 25 and 200°C in electrolytes other than NaCl at ionic strengths up to 7.0.

The solubility of $CaSO_4 \cdot XH_2O$ is:

$$CaSO_4 \cdot XH_2O \rightleftharpoons Ca^{++} + SO_4{}^{=} + XH_2O$$

from which the thermodynamic solubility product is obtained:

$$K^{o}_{sp} = \left[\underline{m}_{Ca^{++}}\right]\left[\underline{m}_{SO_4{}^{=}}\right]\left[\gamma_{Ca^{++}}\right]\left[\gamma_{SO_4{}^{=}}\right]\left[a_{H_2O}\right]^{X}$$

where:

$\underline{m}_{Ca^{++}}, \underline{m}_{SO_4}$ = are molal concentrations,

$\gamma_{Ca^{++}}, \gamma_{SO_4}$ = are activity coefficients,

a_{H_2O} = the activity of H_2O in the solution,

X = the number of moles of H_2O in the solid hydrate.

Using the Debye-Hückel theory, taking the logarithm and rearranging, the solubility quotient is found:

$$\log K_{sp} = \log K^{o}_{sp} + 8\mathcal{S}\left[\frac{I^{1/2}}{1 + A\, I^{1/2}}\right] - X \log a_{H_2O}$$

where:

K_{sp} = the solubility quotient

K^{o}_{sp} = the thermodynamic solubility product

$\mathcal{S}$ = the limiting Debye-Hückel slope

A = a constant (taken as 1.5)

I = the ionic strength

The measured values were well correlated when $A = 1.5$ was chosen. The terms for a_{H_2O} drop out when anhydrite is the solid of interest. Activities of water, a_{H_2O}, for NaCl solutions have been published by Robinson and Stokes(39).

The measured and correlated data are shown in Figures V-A4-1 and V-A4-2 from Marshall, Slusher and Jones' paper. From Figure V-A4-1 the Debye-Hückel slope can be determined from the ionic-strength function. From Figure V-A4-2 the thermodynamic solubility product K^o_{sp} can be found at any given temperature. Using these values and the proper a_{H_2O}, the solubility coefficient K_{sp} of a desired form of calcium sulfate can be calculated at a given temperature in a solution of a given ionic strength.

These calculations have been made for sea water and concentrated sea waters and the results are shown in Figure V-A4-3 for anhydrite and in Figure V-A4-4 for gypsum. In both figures, the solubility product (Ca^{++}) $(SO_4^{=})$ is plotted as a function of the concentration factor (normal sea water C F = 1.0), with temperature as a parameter.

It is interesting to note that both gypsum and anhydrite pass through solubility maxima at several times sea water concentration. Also apparent is the extreme sensitivity of the anhydrous calcium sulfate to temperature, and the relative temperature insensitivity of the dihydrate.

It is also quite apparent that the effect of the other ions in solution (the ionic strength) cannot be ignored and that the solubilities of the various forms of calcium sulfate in pure water solutions is not a reliable guide.

A line of constant ionic ratio can be drawn in Figure V-A4-3 which indicates the concentration or dilution of sea water without a change in composition. The intersection of this line with the solubility lines are the temperatures at which a sea water of a given concentration just becomes saturated with anhydrite. Concentrations at temperatures not plotted can be cross-plotted or determined by interpolation.

FIG. V-A4 - 1

VARIATION OF ACTIVITY (γ) WITH IONIC STRENGTH (I) FOR $CaSO_4$ AND ITS HYDRATES IN $NaCl-H_2O$ (28)

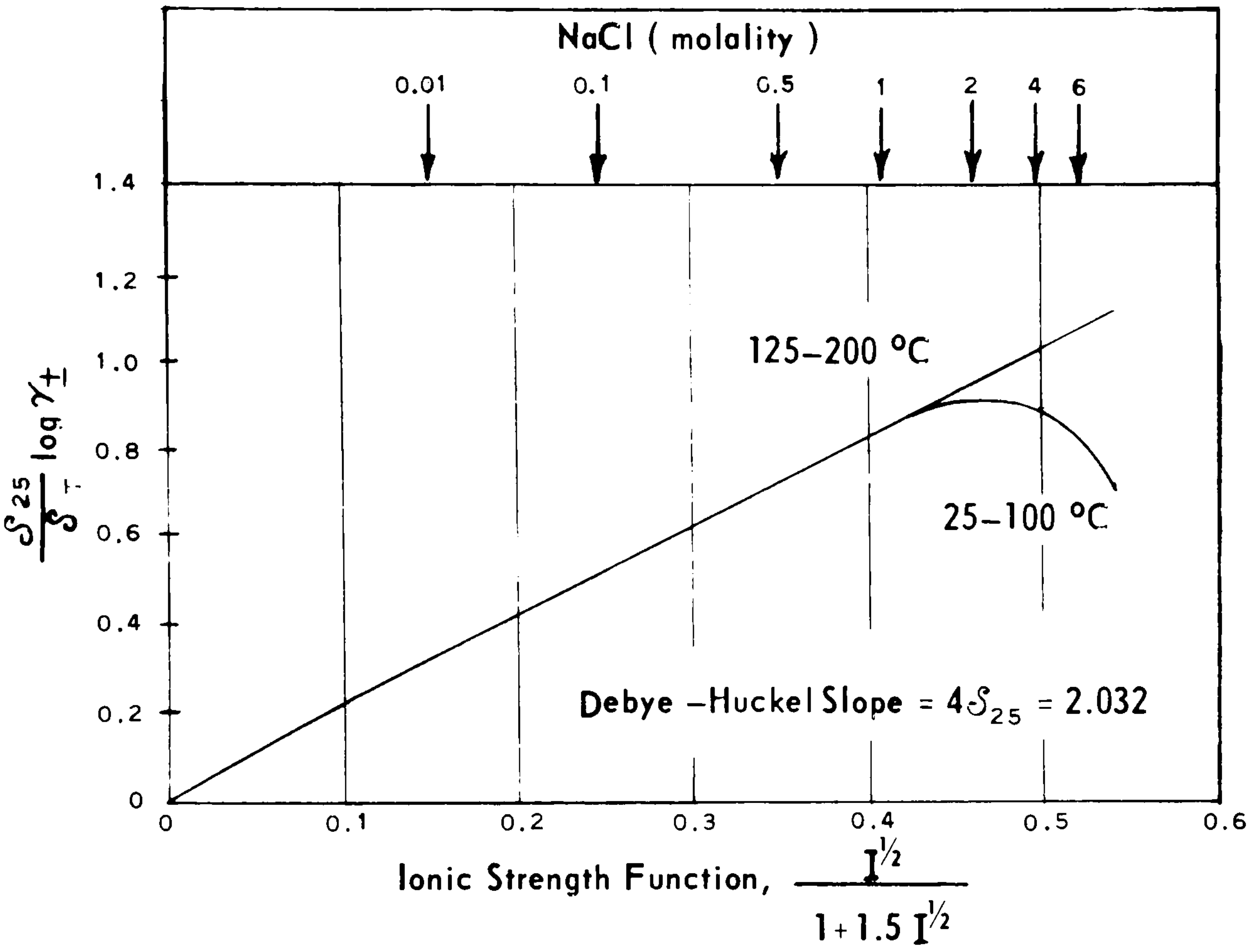


FIG. V-A4-2
THERMODYNAMIC SOLUBILITY PRODUCT OF CALCIUM SULFATE (28)

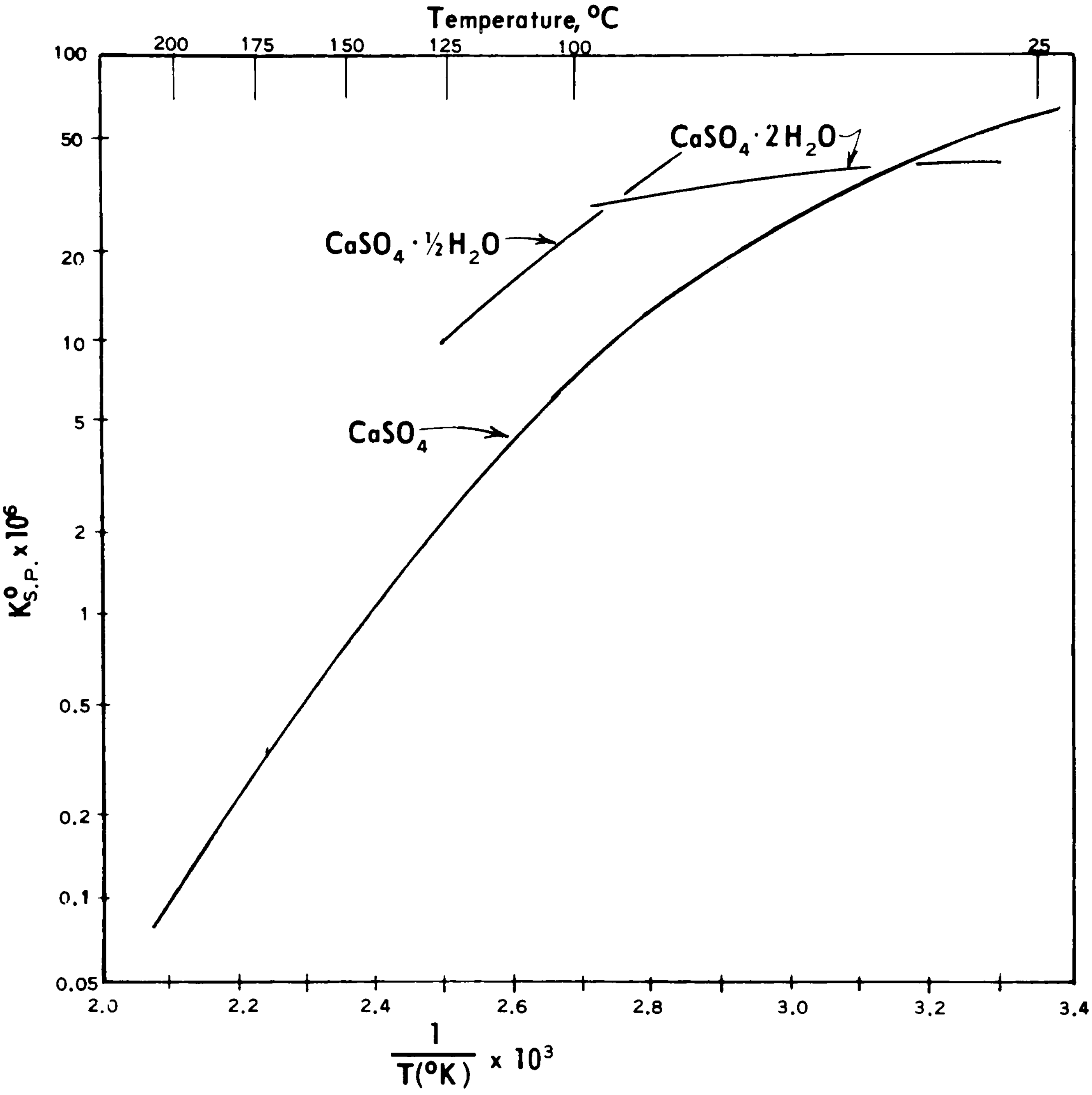


FIG. V-A4 – 3

SOLUBILITY OF CALCIUM SULFATE ANHYDRITE IN CONCENTRATED SEAWATERS

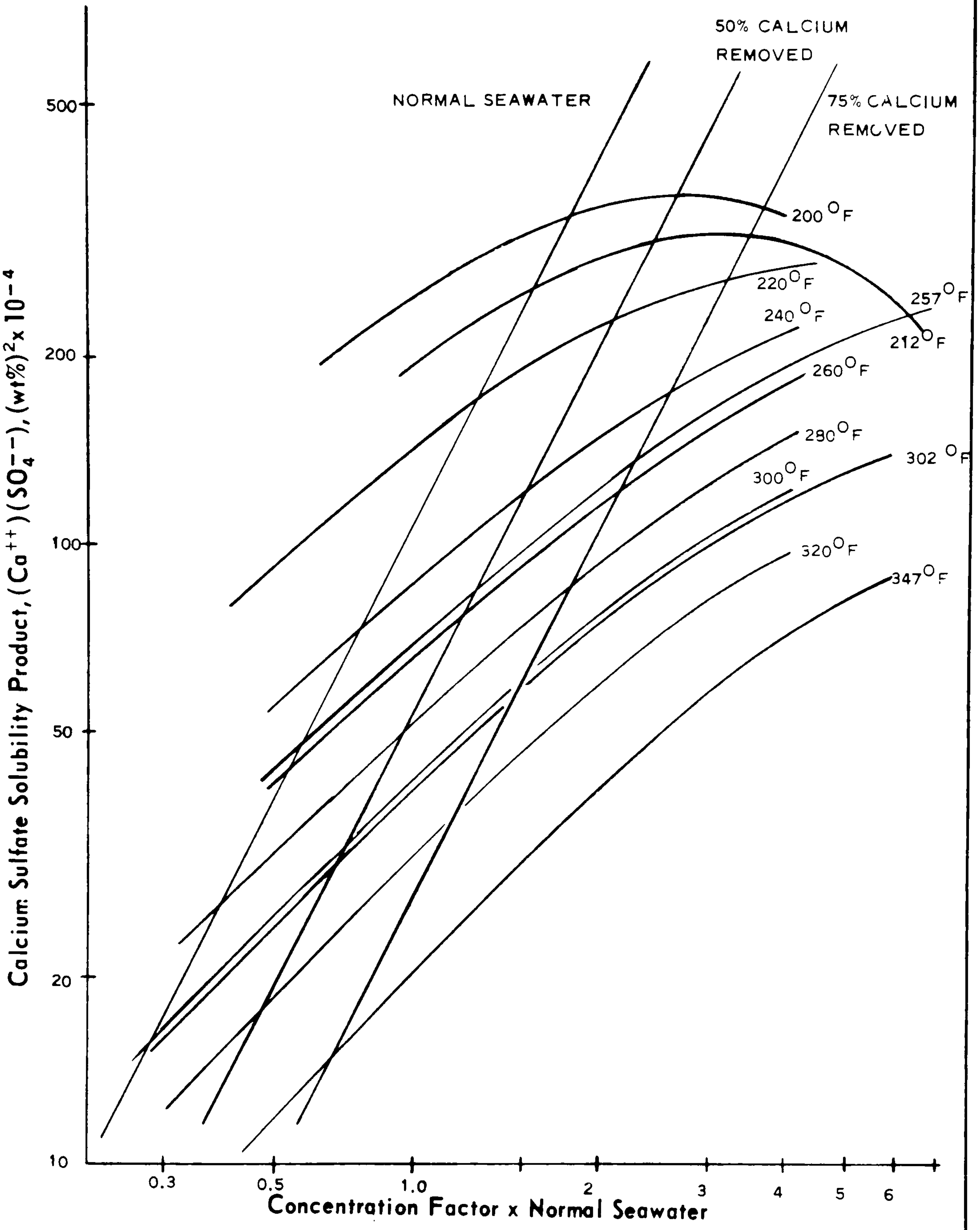
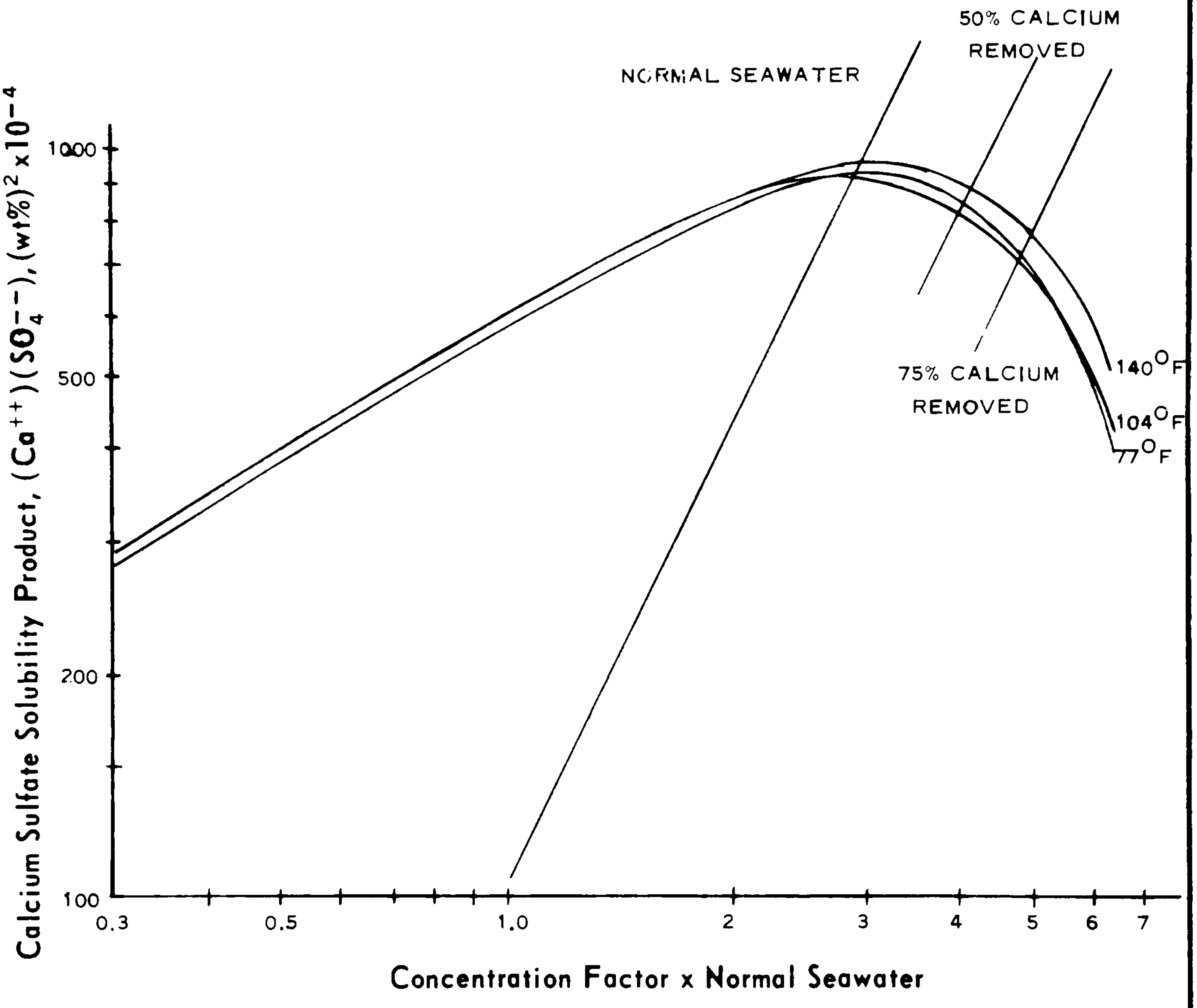


FIG. V-A4 – 4

SOLUBILITY OF GYPSUM IN CONCENTRATED SEAWATER



These values are plotted in Figure V-A4-5 in which the concentration factor of the concentrated (or diluted) sea water is plotted against the temperature of the brine. In this Figure, the lowest lines are the temperatures and concentrations to which sea water can be carried without calcium sulfate precipitation.

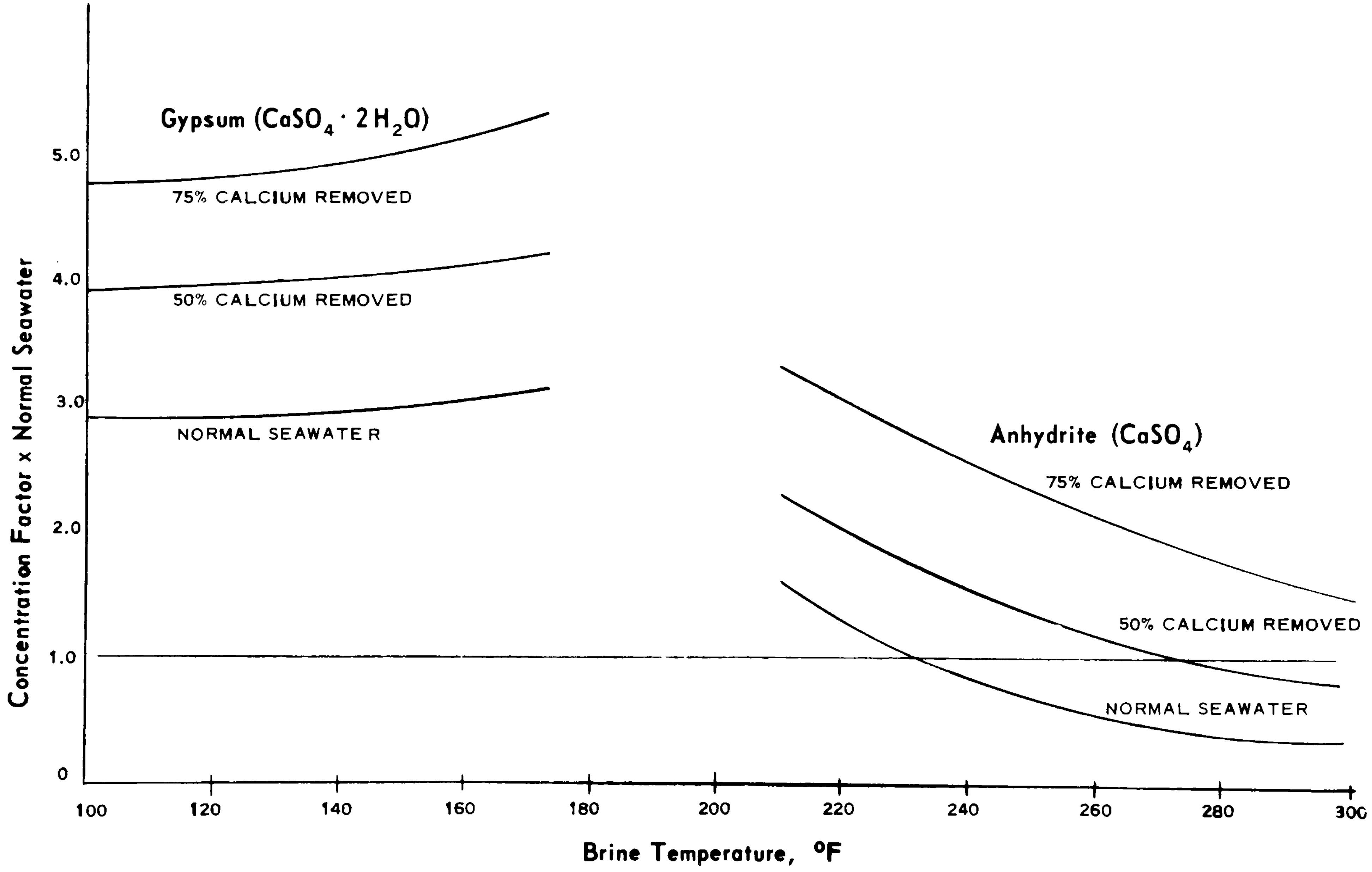
If either calcium or sulfate is removed from the sea water, the solubility product is changed and the concentration-temperature relationship is altered. Lines have been drawn in Figure V-A4-3 for sea waters in which 50 per cent and 75 per cent of the calcium have been removed. The intersections with the solubility lines have been replotted in Figure V-A4-5 to give the concentrations and temperatures to which the softened sea waters can be carried before the solubilities of either anhydrite or gypsum are exceeded.

It is known that in the temperature range between 180°F and about 220°F, the metastable hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$) is the crystalline scale form ordinarily encountered. This form is more soluble at a given temperature than either gypsum or anhydrite, and is not important as a scale in the present method of operation of the Freeport Conversion Plant.

It should be noted that Figures V-A4-3, V-A4-4, and V-A4-5 are for the solubilities of the various forms of calcium sulfate at equilibrium between the solutions and the solid phases. They show the safe operating area within which scale formation cannot be expected. Operation outside of these areas depends upon the kinetics of nucleation and crystal growth, and is possible although such operation is unlikely with the long-tube, vertical, falling-film, evaporative process.

The curves of Figure V-A4-5 have been checked with all available data on the solubilities of anhydrite or gypsum in concentrated sea waters. Some of the references are shown in Figure V-A4-5. Agreement with the curves, in general, is quite good despite the obvious difficulty in obtaining meaningful solubility data at high temperatures in a temperature-dependent system.

FIG. V–A4–5
SOLUBILITY OF CALCIUM SULFATE IN CONCENTRATED SEAWATERS AT VARIOUS TEMPERATURES (28) (35) (4)



b. Plant Scaling Experience

During the more than three years of operation of the Freeport Conversion Plant, 23 analyses have been made of various scales by the Dow Chemical Company. These analyses are shown in Table V-A-4-I. All analyses were by X-ray diffraction.

All five expected types of scale have been found: calcium carbonate, magnesium hydroxide, and three forms of calcium sulfate - gypsum, hemihydrate, and anhydrite.

Aragonite (calcium carbonate) was found only when a magnesium hydroxide slurry was being recycled, when acid was not being added before degassing (samples of 5/25/61).

Alkaline scales were found in the higher temperature effects through 6/20/62 and are probably indicative of inefficient deaeration. No alkaline scales have been found in any samples since this time.

Anhydrous calcium sulfate has appeared with monotonous regularity as the principal constituent of scales from the higher temperature effects and has been found as far down the system as Effect IV when a 250°F first effect brine temperature was attempted. Anhydrite is the principal, and in most cases the only scale compound found in Effect I.

Gypsum has appeared with equal regularity in the lower temperature effects and has been found in Effect X when a concentration factor of four in Effect XII was attempted.

Quartz, the principal crystalline form of the sea-water silt, was found in a majority of the analyses as a minor or trace component. Magnetite, the iron oxide formed when O_2 is restricted, also occurred as a minor constituent.

It can be concluded that the loss of heat-transfer efficiency in the first effect is caused by the formation of anhydrite and the loss of efficiency in Effects XI and XII is caused by the formation of gypsum.

TABLE V-A-4-I

ANALYSES OF SCALES AT FREEPORT LTV DEMONSTRATION PLANTS (X-Ray Diffraction)

Date	Place Taken	Compounds	Formula	Amount
5/25/61	Deaerator (Down stream of control valve)	Aragonite	$CaCO_3$	Only
5/25/61	Sediment (Product water)	Magnesium Hydroxide	$Mg(OH)_2$	Major
		Magnetite	Fe_3O_4	Major
5/25/61	Thickener Slurry	Magnesium Hydroxide	$Mg(OH)_2$	Major
		Quartz	SiO_2	Minor
6/13/61	Effect III (Tubes)	Magnesium Hydroxide	$Mg(OH)_2$	Major
		Anhydrite	$CaSO_4$	Minor
		Quartz	SiO_2	Minor
		Hematite	Fe_2O_3	Minor
6/13/61	Effect IV (Tubes)	Magnesium Hydroxide	$Mg(OH)_2$	Major
		Anhydrite	$CaSO_4$	Minor
		Quartz	SiO_2	Minor
		Magnetite	Fe_3O_4	Minor
6/13/61	Effect X (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Major
		Quartz	SiO_2	Minor
6/13/61	Effect XI (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Major
		Magnetite	Fe_3O_4	Minor

TABLE V-A-4-I
(con't)

Date	Place Taken	Compounds	Formula	Amount
6/13/61	Effect XII (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Only
6/13/61		Magnetite	Fe_3O_4	Major
		Quartz	SiO_2	Major
		Magnesium Hydroxide	$Mg(OH)_2$	Major
		Gypsum	$CaSO_4 \cdot 2H_2O$	Minor
		Hemihydrate	$CaSO_4 \cdot 1/2H_2O$	Minor
6/13/61	P47 Pump (Deaerator)	Magnetite	Fe_3O_4	Major
		Magnesium Hydroxide	$Mg(OH)_2$	Major
		Quartz	SiO_2	Minor
3/8/62	Effect I (Tubes)	Magnesium Hydroxide	$Mg(OH)_2$	Major
		Anhydrite	$CaSO_4$	Large
		Magnetite	Fe_3O_4	Minor
3/8/62	Effect XII (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Only
6/20/62	Effect XII (Distributor Plate)	Quartz	SiO_2	Major
		Magnetite	Fe_3O_4	Minor
		Magnesium Hydroxide	$Mg(OH)_2$	Minor
		Unidentified (Probably Clay)	-	Present
6/20/62	Effect II (Tubes)	Anhydrite	$CaSO_4$	Major
		Magnesium Hydroxide	$Mg(OH)_2$	Minor
		Magnetite	Fe_3O_4	Minor
		Quartz	SiO_2	Minor

TABLE V-A-4-I
(con't)

Date	Place Taken	Compounds	Formula	Amount
7/14/62	Effect VI (Tubes)	Amorphous to X-ray optical emission indicates silicon	(Probably clay silt)	-
9/11/62	Effect I (Strainer)	Quartz	SiO_2	Major
		Anhydrite	$CaSO_4$	Minor
		Feldspar silicate	-	Minor
9/11/62	Effect XII (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Only
1/4/63	Effect I (Tubes)	Anhydrite	$CaSO_4$	Major
		Quartz	SiO_2	Trace
1/4/63	Effect XI (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Major
		Quartz	SiO_2	Trace
1/4/63	Effect XII (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Only
5/23/63	Effect I (Tubes)	Anhydrite	$CaSO_4$	Major
		Quartz	SiO_2	Trace
5/23/63	Effect XII (Tubes)	Gypsum	$CaSO_4 \cdot 2H_2O$	Major
		Quartz	SiO_2	Trace
9/27/63	Effect I (Tubes)	Anhydrite	$CaSO_4$	Only

The operating logs were searched for periods of known scale formation. Operating data for typical periods are shown in Figure V-A4-6. The solubility limits of Figure V-A4-5 for gypsum and anhydrite in normal and concentrated normal sea waters are shown.

The data of 12/6/62 are from typical operation during a high-temperature, high-production run. The second annual report of Stearns-Roger Corporation(48) says for this period:

"Scale formation in Effects I and XII as evidenced by excessive carry over from Effect XII and elevated temperature differentials across Effects I and XII, confirmed that an extensive outage would be necessary for the cleaning, inspection, and modifications. It became necessary to reduce Plant production to maintain the Effect I vapor temperature at, or less than, the 251°F design maximum and to minimize carry over from Effect XII.

"Inspection of the bottoms of all evaporators for scaling disclosed that the tubes in Effect I had minimal deposits; Effect XI had 76 tubes showing heavy gypsum scale; and Effect XII exhibited heavy deposit at the bottom of approximately 80% of the tubes, 115 of which were plugged solidly."

Data from April 9, 1963, (during a month in which a record production was established):

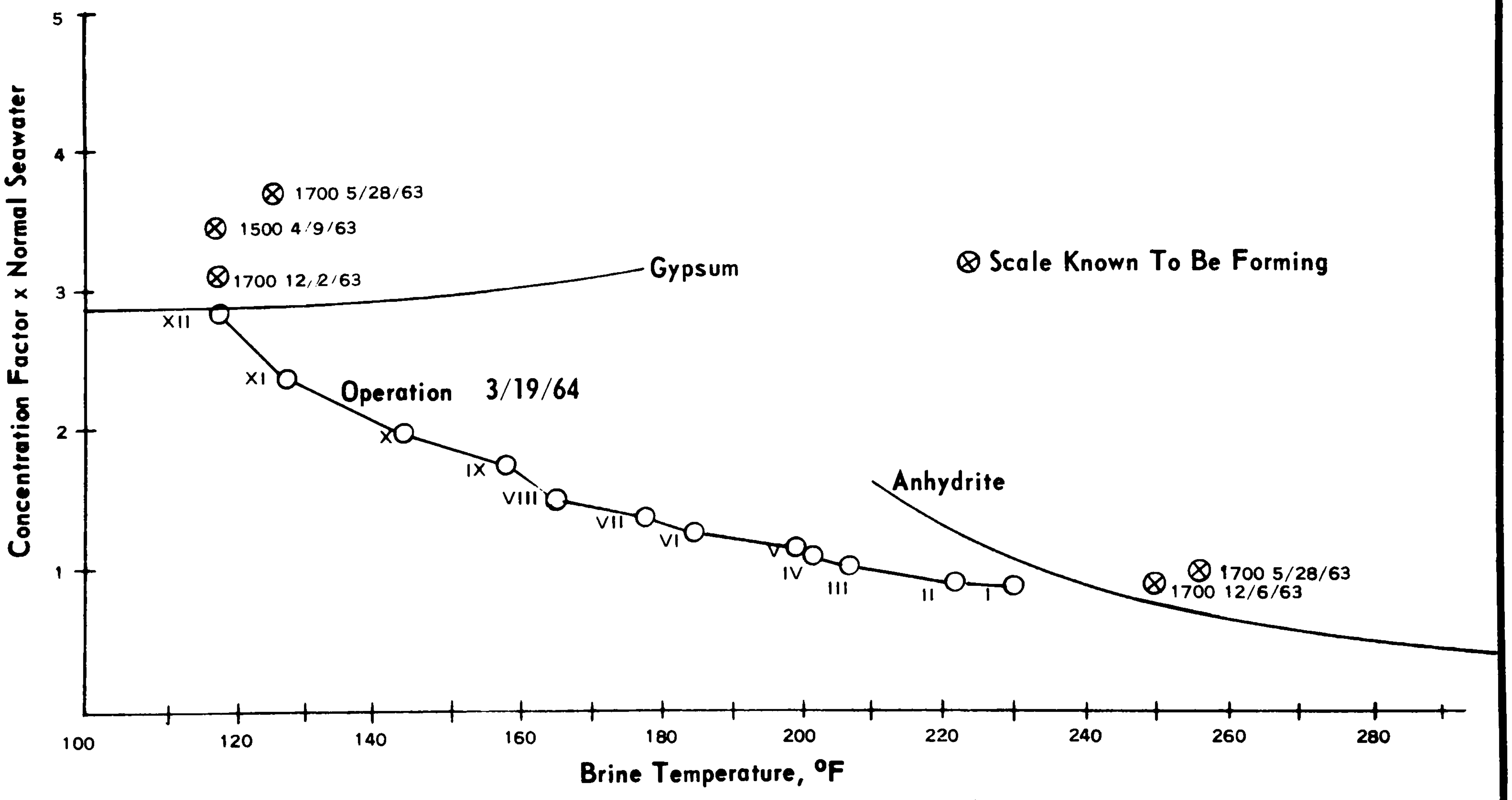
"Freeport product conductivity increased from 25 ppm sodium chloride to slightly greater than 100 ppm. This increased carry over, combined with the increased temperature differential across Effect XII indicated a scale buildup in this Effect."

Data from May 28, 1963, during the maximum production run:

"Operating conditions, concentration of Effect XII brine, 3.8 maximum, Effect I vapor temperature 250°F maximum.

"Continuous operation at these ratings could not possibly be maintained over an extended period, inasmuch as scale buildup in Effect XII would necessitate a reduction in rate."

FIG. V-A4-6
OPERATION AND SCALING CONDITIONS
FREEPORT LTV FALLING FILM
DEMONSTRATION PLANT



Both the operations of 5/28/63 and 12/6/63 indicated the presence of scale in the first effect: both were attempted at 250°F. These points exceed the solubility of anhydrite in the heated feed sea water. Precipitation of anhydrite is to be expected.

All operations at Effect XII brine concentration factors exceeding three have been accompanied by the formation of gypsum.

Also shown in Figure V-A4-6 is the temperature and concentration of the brines in each effect as measured on March 19, 1964. No appreciable scale was being formed, and according to the solubilities, none was to be expected.

It can be concluded that operation of the Freeport Conversion Plant is limited to temperatures of the brine in Effect I of less than 240°F and Effect XII brine concentrations of less than three concentration factor if scaling is to be prevented and normal sea water is fed.

More dilute sea waters can be raised to higher first effect temperatures without scale formation, but if concentration factors are based on normal sea water and not on fed sea water, the brine concentration in Effect XII cannot be increased beyond three.

Operation of the long-tube, vertical, distillation plant in supersaturated regions for extended periods is unlikely.

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

5. Ion-Exchange Softening Design

a. Ion-Exchange Equilibria

If either calcium or sulfate can be removed from the feed solution to the evaporator, then the solubility product is less than in the original raw sea water and the treated water can be heated to a higher temperature and more water can be removed to give a higher output brine concentration.

A cation-exchange resin, such as Dowex 50, can partially remove calcium from the feed sea water and the resin can be regenerated by the concentrated evaporator blowdown. The full calcium concentration does not enter the evaporation circuit, but part of the calcium bypasses the evaporator on the resin and leaves in the regenerant.

The softening of sea water as a pretreatment for saline water conversion processes has been patented(37).

The process has been tested successfully by the Dow Chemical Company under contract number 14-01-0001-205 with the Office of Saline Water and has been reported(35).

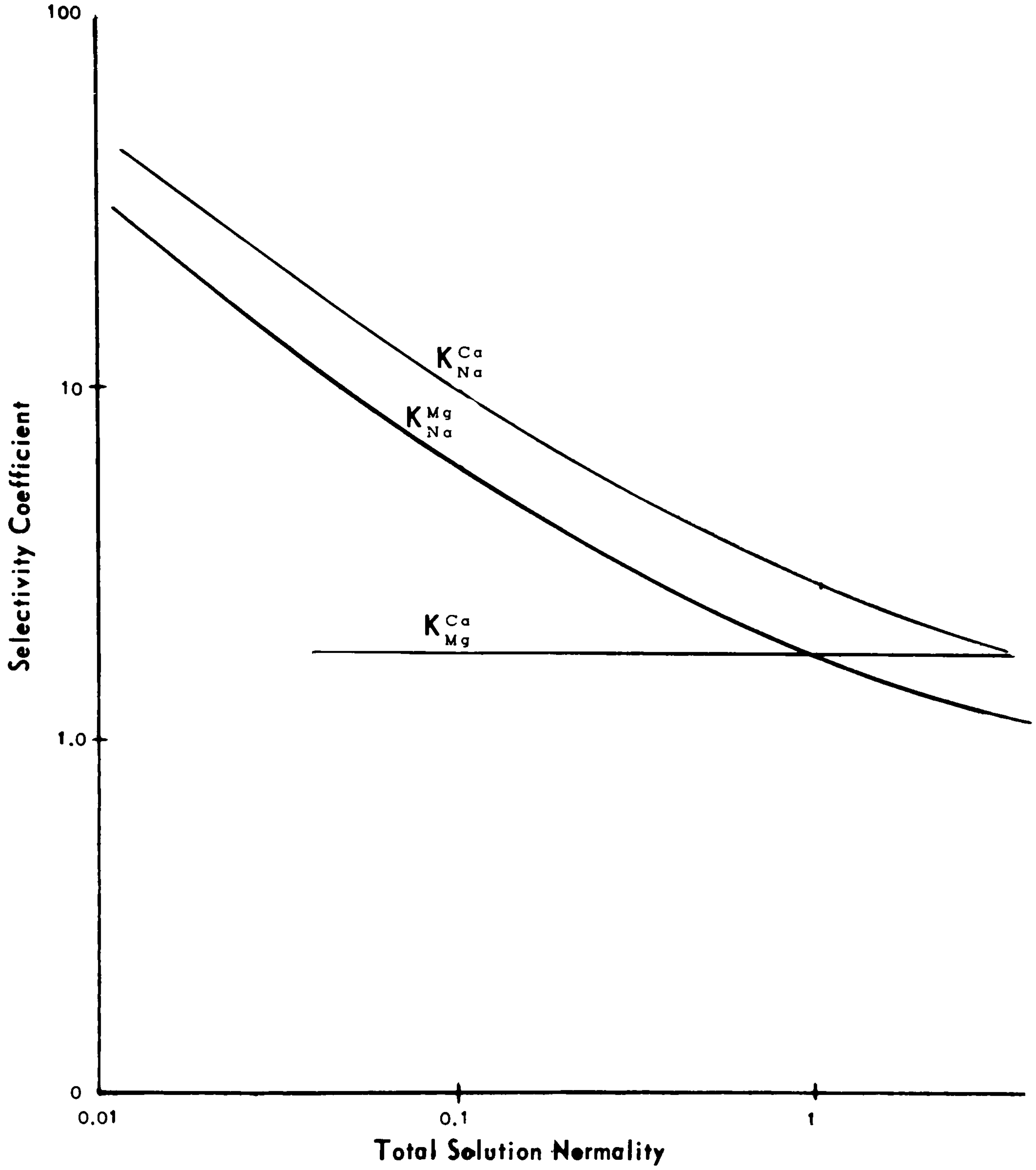
Careful design of an ion-exchange unit requires knowledge of the ion-exchange equilibria in the system to be designed. The sea water - resin equilibria has been reported previously(36).

The system of interest is a ternary ionic equilibria with Ca^{++}, Mg^{++}, and Na^{+} competing for sites on the resin. All three ions must be considered in the design. Although Mg^{++} is no longer harmful as a scale former when the alkalinity has been removed from the sea water, it is still important to the exchange equilibria.

The variation in selectivity coefficient with total solution normality is shown in Figure V-A5-1. Only the two mono-divalent ion-exchanges are concentration dependent. The Ca^{++}-Mg^{++} exchange is not affected by the concentration of the solution.

FIG. V-A5 – 1

VARIATION IN SELECTIVITY COEFFICIENT WITH TOTAL SOLUTION NORMALITY (36)



The selectivity coefficients fit the equations:

$$1/2\ MgS + NaR \rightleftharpoons 1/2\ MgR + NaS$$

$$1/2\ CaS + NaR \rightleftharpoons 1/2\ CaR + NaS$$

$$1/2\ CaS + 1/2\ MgR \rightleftharpoons 1/2\ CaR + 1/2\ MgS$$

and are:

$$K^{Ca}_{Na} = \left[\frac{X^{Ca}_{R}}{X^{Ca}_{S}}\right]^{1/2} \left[\frac{X^{Na}_{S}}{X^{Na}_{R}}\right]$$

$$K^{Mg}_{Na} = \left[\frac{X^{Mg}_{R}}{X^{Mg}_{S}}\right]^{1/2} \left[\frac{X^{Na}_{S}}{X^{Na}_{R}}\right]$$

$$K^{Ca}_{Mg} = \left[\frac{X^{Mg}_{R}}{X^{Ca}_{S}}\right]^{1/2} \left[\frac{X^{Mg}_{S}}{X^{Mg}_{R}}\right]^{1/2}$$

where:

X^{Ca}_{R} is the equivalent fraction of calcium on the resin

$$\frac{(\text{equivalents } Ca^{++})}{\text{total capacity}}$$

X^{Ca}_{S} is the equivalent fraction of calcium in the solution

$$\frac{(\text{equivalents } Ca^{++})}{\text{solution normality}}$$

and:

$$X^{Ca}_{R} + X^{Na}_{R} + X^{Mg}_{R} = \sum X_{R} = 1$$

$$X^{Ca}_{S} + X^{Na}_{S} + X^{Mg}_{S} = \sum X_{S} = 1$$

From these equations and the selectivity coefficients from Figure V-A5-1, the resin composition can be calculated if the solution composition and concentration are known, and vice versa.

Given:

X_S^{Na}, X_S^{Ca}, X_S^{Mg}, Total concentration

K_{Na}^{Ca}, K_{Na}^{Mg} From Figure V-A5-1

Then: $X_R = 1$

$$X_R^{Na} + \left[K_{Na}^{Ca}\right]^2 \left[\frac{X_R^{Na}}{X_S^{Na}}\right]^2 X_S^{Ca} + \left[K_{Na}^{Mg}\right]^2 \left[\frac{X_R^{Na}}{X_S^{Na}}\right]^2 X_S^{Mg} = 1$$

The real quadratic root is:

$$X_R^{Na} = \frac{-1 + \sqrt{1 + 4A}}{2A}$$

$$A = \left[K_{Na}^{Ca}\right]^2 \frac{X_S^{Ca}}{\left[X_S^{Na}\right]^2} + \left[K_{Na}^{Mg}\right]^2 \frac{X_S^{Mg}}{\left[X_S^{Na}\right]^2}$$

and:

$$X_R^{Ca} = \left[K_{Na}^{Ca}\right]^2 \frac{X_S^{Ca}}{\left[X_S^{Na}\right]^2} \left[X_R^{Na}\right]^2$$

$$X_R^{Mg} = \left[K_{Na}^{Mg}\right]^2 \frac{X_S^{Mg}}{\left[X_S^{Na}\right]^2} \left[X_R^{Na}\right]^2$$

From these calculated equilibria, a plot of the equivalent fraction of calcium on the resin can be made against the equivalent fraction of calcium in the solution. This has been done for various total solution concentrations and various calcium fractions in solution and is shown in Figure V-A5-2.

It should be recognized that these plots are for calcium in sea water and concentrated sea waters only and that similar sets exist for Mg^{++} and Na^{+} and can be constructed from the same data.

In Figure V-A5-2 are shown the equilibrium lines for normal sea water and sea waters of various concentration factors. The difference between

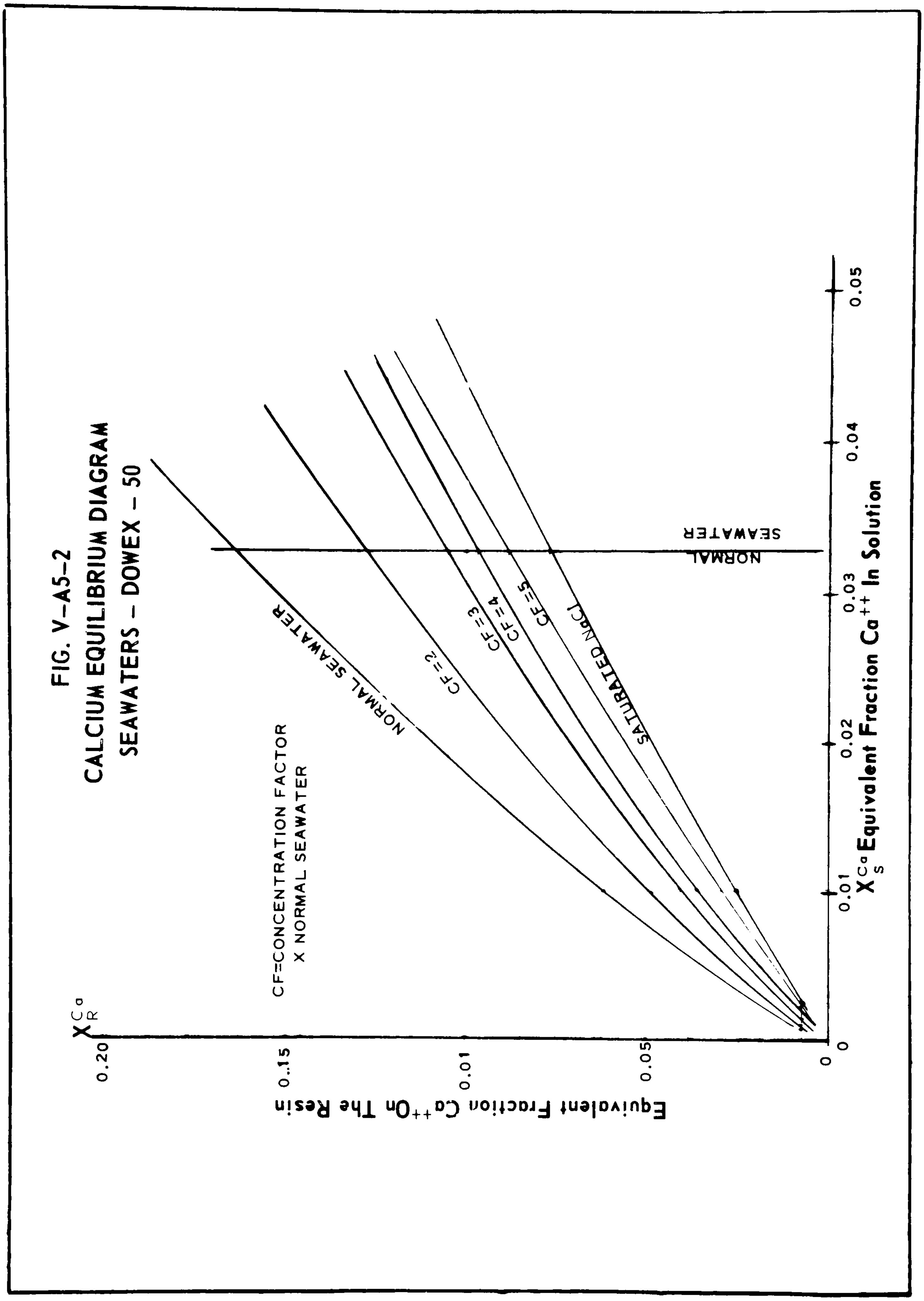


FIG. V-A5-2
CALCIUM EQUILIBRIUM DIAGRAM
SEAWATERS - DOWEX - 50

the equivalent fractions of calcium on the resin X_R^{Ca} in equilibrium with sea water and in equilibrium with a concentrated sea water is the amount of calcium that can be removed from a given volume of solution by a given volume of resin. The more concentrated the solution, the more effective is the regeneration. The less concentrated the sea water, the more effective is the softening.

b. Design Conditions

Two conditions were chosen for the ion-exchange design. Removal of 50 per cent of the calcium from the feed sea water will allow heating to 275°F without anhydrite precipitation. This condition can be met in a single-stage, sea-water resin softening, if the resin is regenerated with brine at a four-times concentration factor in a fixed bed. This system has been thoroughly tested in a pilot plant.

300°F was chosen as the maximum temperature at which the existing Freeport Conversion Plant can be safely operated. Both the original bid specifications and plant design were for potential operation at 300°F.

Operation at a first-effect brine temperature of 300°F will require removal of about 65 per cent of the calcium from normal sea water and will allow a regenerant brine concentration factor of nearly five in the last effect.

Flows used for the ion-exchange design were those to be expected when the existing plant is operated at a higher Effect I temperature and a more concentrated effluent brine. These flows were taken from the heat and material balances at the two temperatures.

Residence times in the contact columns are taken from prior work(36). Four minutes at a flow of six feet per minute was used.

Temperature has relatively little effect on the ion-exchange equilibria, but it does have an effect on the kinetics of the ion-exchange. The hotter the sea water being treated, the more rapid the exchange. The hotter the brine, the lesser the viscosity and density, and the greater the exchange rate.

The ion-exchange equipment can be located anywhere in the sea-water heating circuit, either before or after the deaerator. Probably the best location is after P-3 and the 312 condenser and before the 214 and 215 exchangers.

All ion-exchange designs have been based on normal sea water as a feed although it is realized that during a majority of the year at Freeport, less than normal sea water will be the feed. In general, the designs are conservative, are designed for the worst expected condition, and operational softening should be better than design.

Dowex 50 W, 50 to 100 mesh, eight per cent cross-linked has been used as the cation resin in the equilibrium design and capital cost estimates.

c. Continuous Cyclone. Fixed Bed Regeneration 275°F

This ion-exchange system was chosen for a first design because it is the process which was piloted on sea water and previously reported(35).

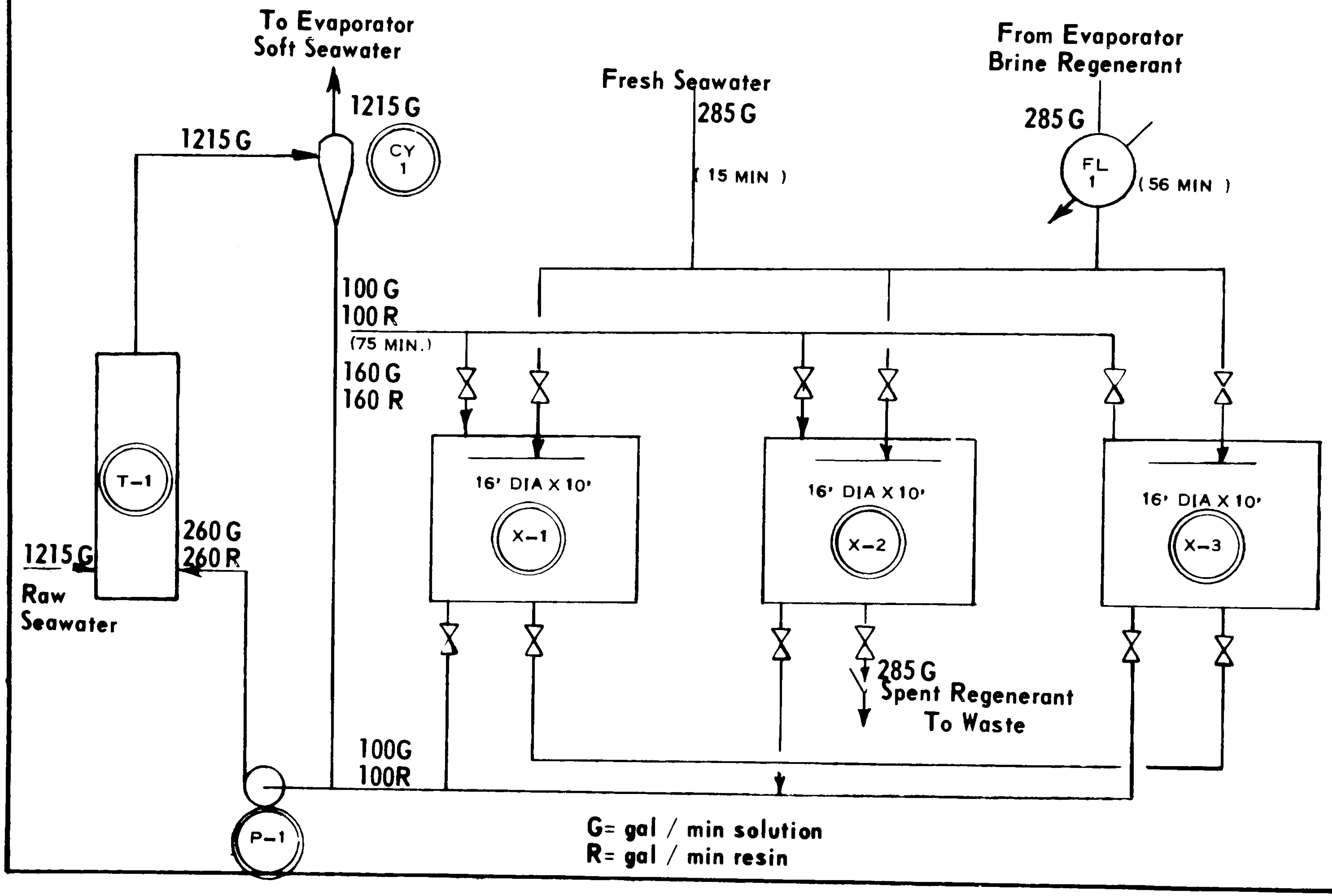
The process flow sheet is shown in Figure V-A5-3. The unit is designed so that the cyclone operates continuously in single-stage equilibrium with the feed sea water to produce a softened sea water and spent resin. The columns are sized so that at any one time, one column is feeding new resin, one column is receiving spent resin, and one or more columns are being regenerated or washed. There must be an integral number of columns. The amount of resin required is decreased as the number of columns increases, but the capital required is increased. The least total investment is the desired condition.

Table V-A-5-I reports the required capital and resin for three, four, and five total columns. It is apparent that the larger number of columns is most economical for this design condition.

d. Continuous Cyclone. Staged Softening and Regeneration, 275°F

Consideration was given to a multiple-staged softening and regeneration in which both softening and regeneration are conducted in concurrent contact columns followed by hydraulic cyclones.

FIG. V-A5 – 3
FLOWSHEET CONTINUOUS CYCLONE
FIXED BED 275 °F



This system has not been pilot planted, but was designed from the resin equilibrium data.

The flow sheet for the 275°F, 50-per-cent calcium-removal condition is shown in Figure V-A5-4. Two softening and two regeneration stages are sufficient when twelve volumes of normal sea water are softened by one volume of resin, and the brine concentrated four times.

The equilibrium diagram is shown in Figure V-A5-5. The circled numbers in Figure V-A5-5 correspond to the circled numbers in the flow sheet.

The incoming raw-feed sea water is mixed with the underflow from the second softening stage at ① and comes into equilibrium with the first-stage softened water at ② The resin from the first stage is forwarded to the second regeneration stage at ⑦ and the first-stage softened water over the cyclone is mixed with freshly regenerated resin at ③ and comes into equilibrium at ④ to form the final softened sea water and the second-stage resin.

The water is evaporated with no change in the ratio of ions so the soft sea water becomes the feed brine to the first regeneration stage at ⑤ where it is mixed with the resin from the second regeneration stage. When equilibrium is reached at ⑥, the regenerated resin is the underflow from the cyclone and the overflow is the feed to ⑦ where it is mixed with the spent resin from ② At point ⑧ the spent regenerant is in equilibrium with the second brine-stage resin. Because there has been no precipitation or accumulation of calcium, the equivalent fraction of calcium in the spent brine must equal that of the raw sea water.

The slope of the lines from points ① to ②, ⑤ to ⑥ etc., are set by the ratio of solution to resin. There is some dilution of the second brine stage by the solution accompanying the spent softening resin, and some increase in concentration in the second softening stage caused by the brine accompanying the regenerated resin. These dilutions and concentrations have been allowed for by the shift of the equilibrium lines.

FIG. V-A5 – 4
ION-EXCHANGE FLOWSHEET
EXTENDED FREEPORT LTV PLANT

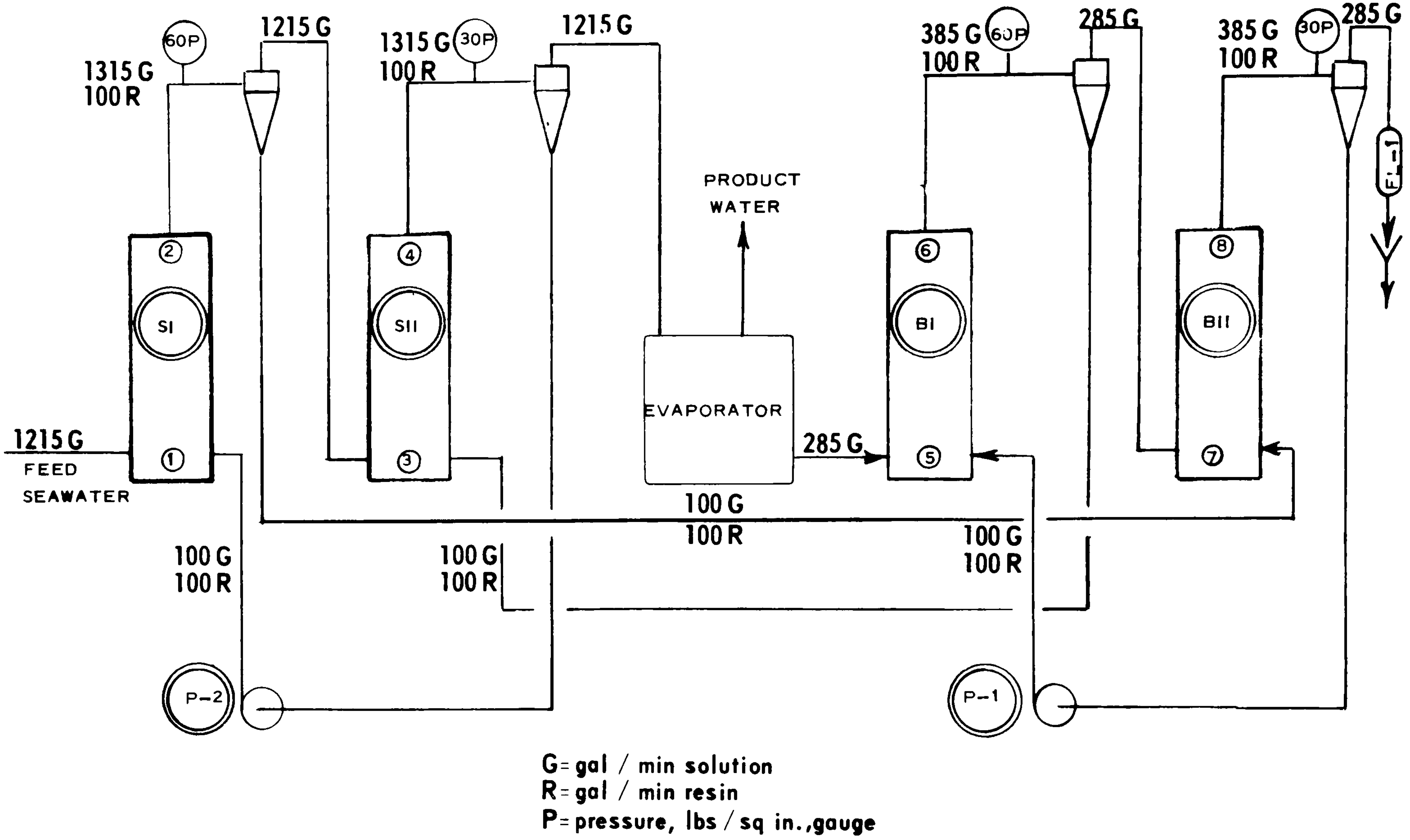
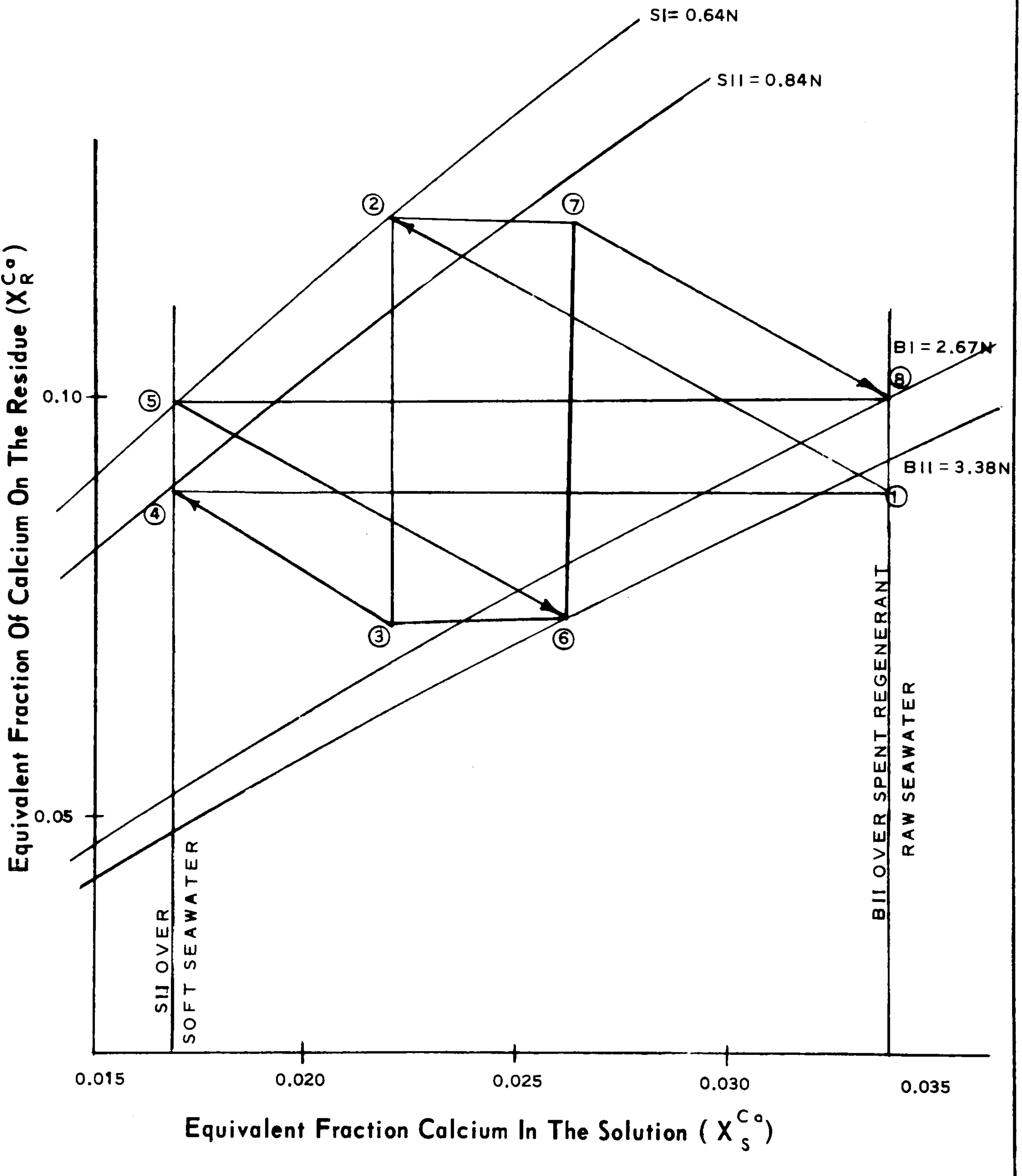


FIG. V-A5-5
SOFTENING AND REGENERATION EQUILIBRIUM DIAGRAM
275 °F OPERATION



Using these diagrams, an estimate has been made of the required capital and amount of resin required. This is compared with the three fixed-bed estimates of the previous sections in Table V-A-5-I. It is apparent that the multiple staging has greatly diminished the amount of capital and amount of resin required to soften an equivalent amount of sea water.

The proposed operation is sound and should present no mechanical or physical problems that have not previously been encountered or solved. The second brine stage will operate close to or above the solubility limit of gypsum. The relatively short retention time in the columns, the turbulent flow, and the presence of the resin should delay gypsum precipitation, but it is recommended that the overflow be diluted to a concentration factor of less than three by the condenser cooling water.

e. Continuous Cyclone. Staged Softening and Regeneration, 300°F

Operation at 300°F requires that about 65 per cent of the calcium be removed from the solution. Because the staged operation was much more economical for the 275°F case, it was the only system studied for 300°F operation.

It was found that two regeneration stages were not sufficient to remove enough calcium at the expected brine concentrations at reasonable resin to solution ratios without additional regenerant. For the extended plant operation, 16 gallons per minute of saturated NaCl brine was required. Although saturated brine is available close to the Freeport plant site, it was felt that this was a specialized, local condition, and not representative of normalized conditions.

Three regeneration stages and two softening stages were able to soften normal sea water sufficiently to prevent precipitation of anhydrite at 300°F without the use of additional regenerant.

The flow sheet is shown in Figure V-A5-6 and the equilibrium diagram in Figure V-A5-7. The circled numbers are equivalent in the equilibrium diagram and on the flow sheet. The normalities correspond to the expected dilutions by the solutions accompanying the underflow resins.

FIG. V–A5–6
ION-EXCHANGE FLOWSHEET
EXTENDED FREEPORT LTV PLANT

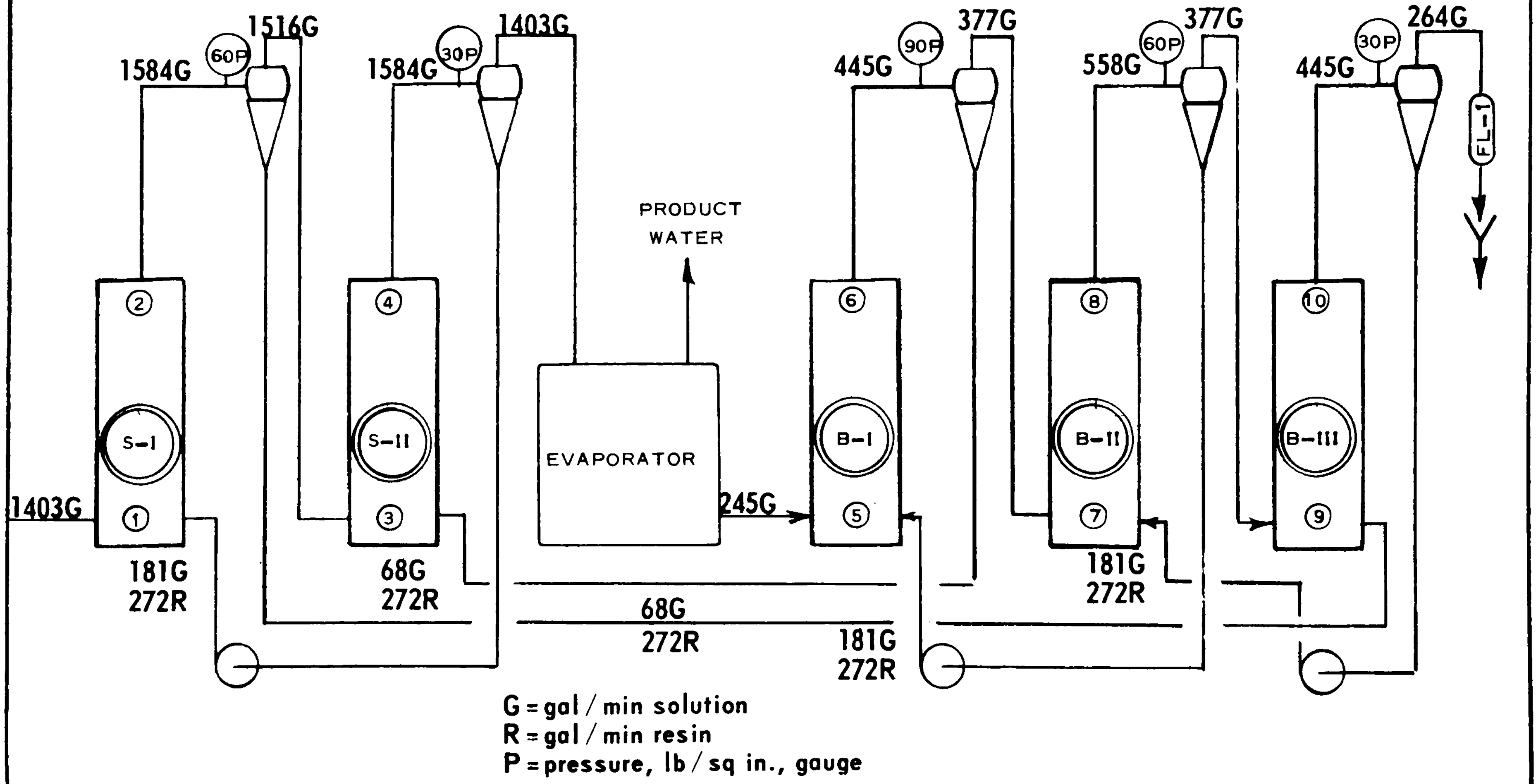
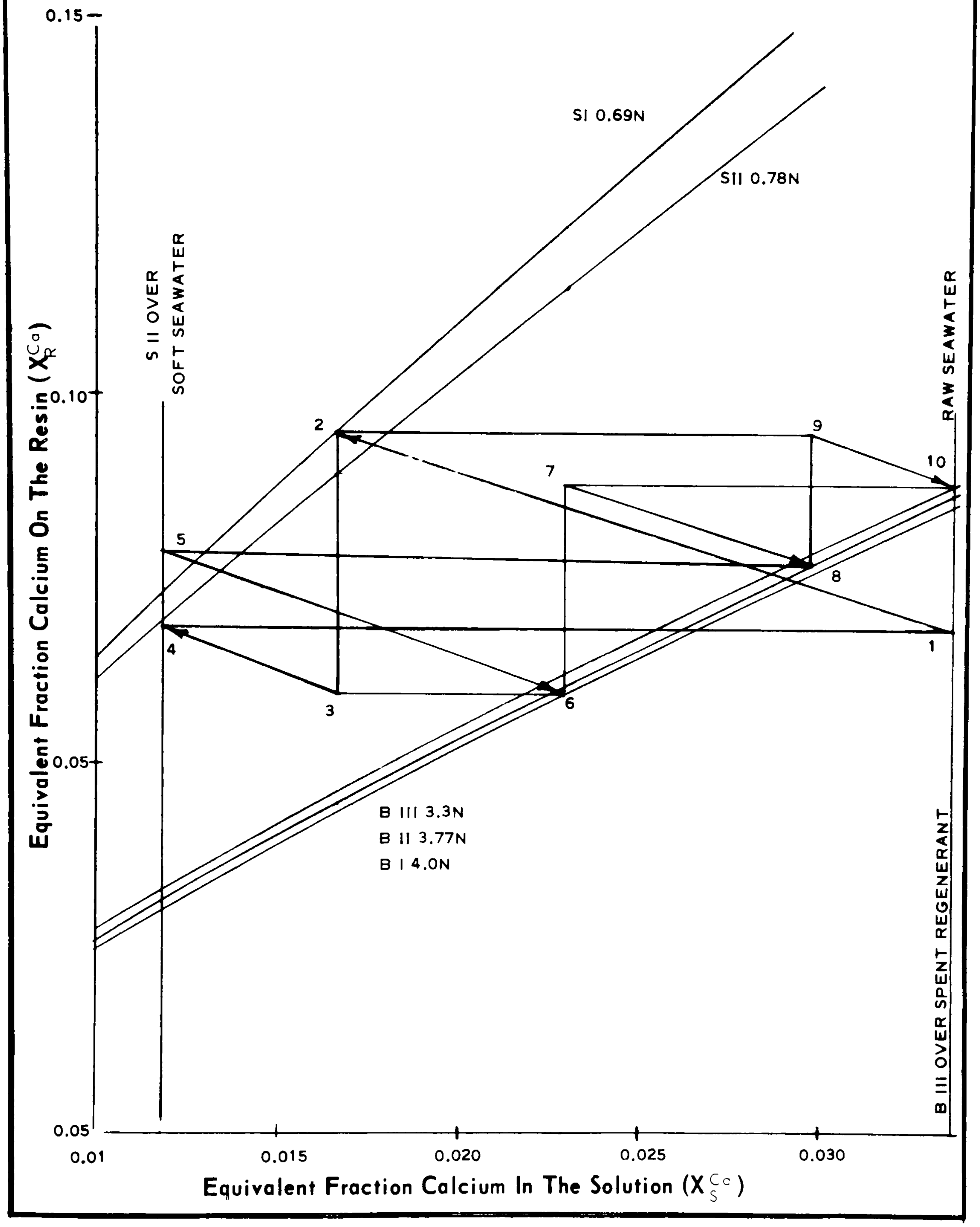


FIG. V-A5-7

SOFTENING AND REGENERATION EQUILIBRIUM DIAGRAM
FOR 300°F OPERATION



The cyclone splits were taken so that the first-stage softening cyclone (SI) and the first and second-stage regeneration cyclones (BI and BII) were operated to produce a low-water-content underflow at some inefficiency in resin recovery. The second-stage softening and third-stage brine cyclone splits were taken for more efficient resin recovery. An in-line solids separator is used as protection against resin leaving the system in the brine cyclone overflow.

The equipment schedule and ion-exchange capital cost for the extended 300°F operation is shown in Table V-A-5-I.

The capital and resin requirements are compared in Table V-A-5-II.

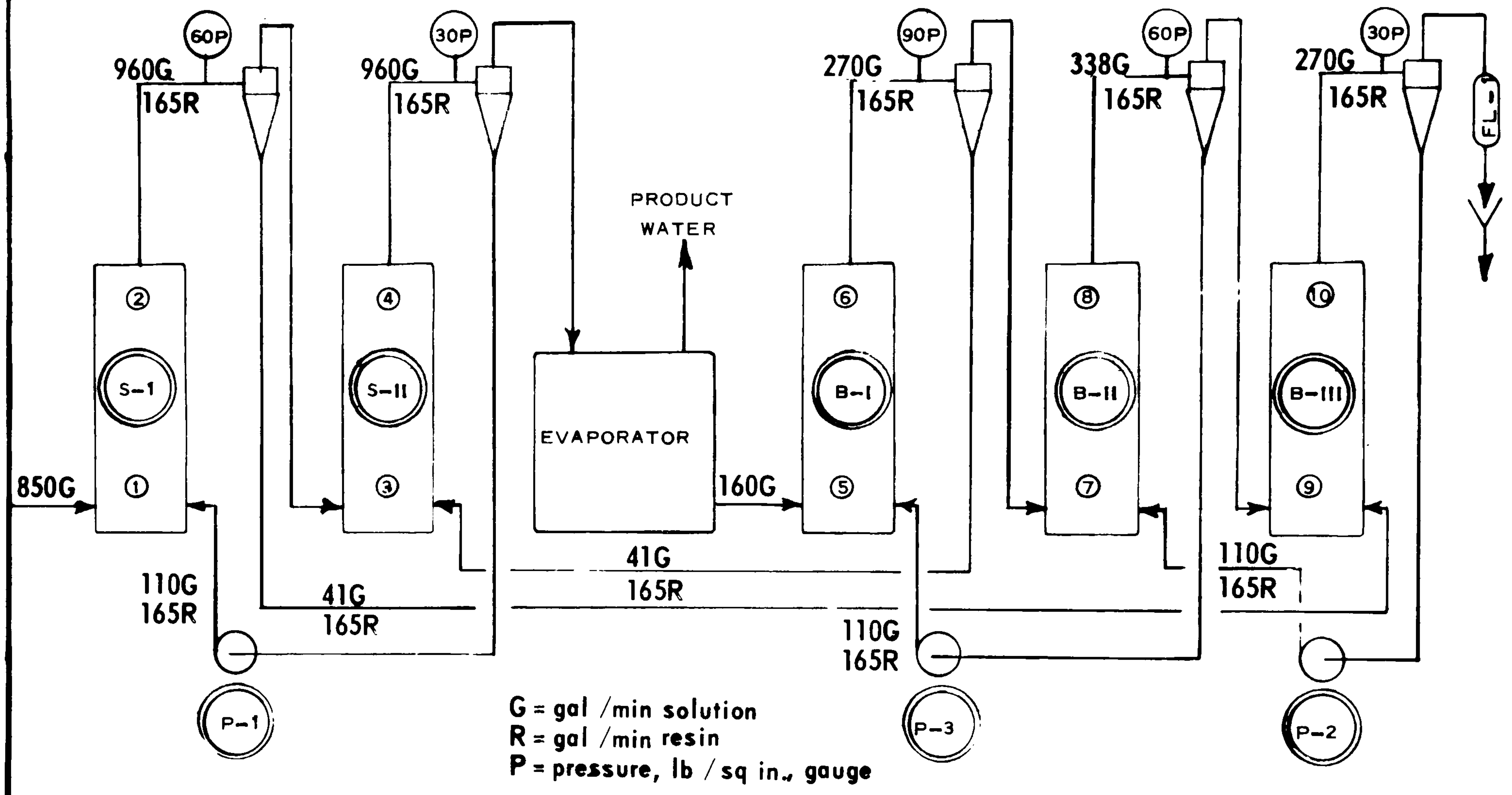
f. Normalized Plant

The most economical method of operation of those studied was the 300°F operation using two softening and three regeneration stages.

The ion-exchange softening system for the normalized one-million-gallon-per-day plant was designed from the same equilibrium diagram as the 300°F revised Freeport plant flow, with the equipment resized to fit the smaller flow conditions.

The ion-exchange capital is included in the normalized-plant capital estimate. No additional regenerant is required. The flow sheet is shown in Figure V-A5-8.

FIG. V – A5 – 8
ION-EXCHANGE FLOWSHEET
NORMALIZED LTV PLANT 300 °F



G = gal /min solution
R = gal /min resin
P = pressure, lb / sq in., gauge

TABLE V-A-5-I

EQUIPMENT SCHEDULE
300°F EXTENDED OPERATION
CONTINUOUS STAGED CYCLONE

Item Number	Description	Quantity	Total Cost Installed
SI, SII	Column 7-ft diameter x 24-ft steel epoxy lined	2	$ 9,944
BI, BII, BIII	Column 4.5-ft diameter x 24-ft steel epoxy lined	3	8,598
	Erection of Columns		855
SIC, SIIC	24-inch hydraulic cyclone steel, rubber lined	2	1,200
BIC, BIIC, BIIIC	12-inch hydraulic cyclone steel, rubber lined	3	795
PI, PII, PIII	Slurry pump 450 gpm 1750 rpm, 50 hp	3	7,800
FL1	Separator, line solid	1	1,000
Resin	Dowex 50W 50-100 mesh	730 cu ft	17,155
	Placing in Column		176
	Flow indicator	7	2,800
	Pressure indicator	5	125
	Salinity indicator	2	350
	Mount and pipe		1,796
	Foundations		3,400
	Piping		16,000
	Electrical		5,030
	Painting		1,600
	Fees, etc.		7,924
	Total Installed Cost		$86,548

TABLE V-A-5-II

SUMMARY OF ION-EXCHANGE SOFTENING CAPITAL

Case	Process	Plant Size (Gross, gpd)	Temperature, °F	Capital $	cu ft Resin (Included in Capital)
IA	Continuous Cyclone Fixed Bed, 3 columns	1,433,000	275	189,910	4105
IB	Continuous Cyclone Fixed Bed, 4 columns	1,433,000	275	160,688	3080
IC	Continuous Cyclone Fixed Bed, 5 columns	1,433,000	275	157,158	2670
IIA	Continuous Cyclone Staged Regeneration	1,433,000	275	53,415	220
IIIA	Continuous Cyclone Staged (additional regeneration)	1,812,000	300	86,869	500
IIIB	Continuous Cyclone Staged (no additional regenerant)	1,812,000	300	86,548	730
IVA	Continuous Cyclone Staged (normalized plant)	1,000,000	300	67,400	450

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

6. Sea-Water Filtration

Filtration and clarification of the incoming sea water is discussed in Section IV-A. It seems better to design the equipment to handle the silt load in the sea water rather than to design equipment to separate the solids.

The multiple-staged, fluidized, ion-exchange beds will not require filters, either on the raw sea-water feed, or on the regenerant brine stream. Filtration in this case is not necessary.

SECTION V. PROCESS CHEMICAL CONSIDERATIONS

A. Sea Water

7. Review of Badger 300°F Seeding Process

a. Process Description

Calcium sulfate scale formation normally limits the maximum scale-free sea-water evaporation temperature to about 235°F (Figure V-A4-5). Increasing the maximum temperature at which an evaporator can be maintained scale-free, and thus increasing the available temperature difference across the evaporator heat-transfer surface, is an important means of increasing the vapor production rate. The revised 275°F and 300°F process flow sheets included in this report illustrate the point.

In the last eight months of 1963, W. L. Badger Associates, Inc. operated, at the Office of Saline Water Harbor Island Test Station, a pilot plant to develop a means of preventing $CaSO_4$ scale formation at temperatures up to 300°F. The pilot plant and process were designed to duplicate as closely as possible the conditions that would result if the Freeport plant were operated at 300°F(4). This process is being reviewed here at the request of the Office of Saline Water.

The pilot-plant process involved the following steps:

(1) Warming sea water to 135°F.

(2) Decarbonating and deaerating the sea water by steam stripping.

(3) Preheating sea water to approximately 300°F.

(4) Adding to sea water a $CaSO_4$ (anhydrite) seed-crystal slurry, either during preheating or immediately after, to give a seed concentration of two grams per one hundred cubic centimeters.

(5) Passing of this stream through a retention column to afford time for supersaturated $CaSO_4$ to precipitate on the seed crystals.

(6) Feeding retention-column effluent to the long-tube, vertical evaporator. It operated at a boiling point of about 300°F and evaporated about six per cent of the feed.

(7) Further concentrating the long-tube, vertical-evaporator effluent in a forced circulation evaporator to a concentration four times normal sea water. This simulated the remaining eleven effects of a twelve-effect plant.

(8) Passing the resultant slurry through a thickener for recovery of seeds. The underflow was returned to the fourth step. An underflow slurry heater was required if slurry was added after the sea-water preheater.

It was found that scale did not form in the long-tube, vertical-evaporator if the retention-column temperature was slightly above the long-tube, vertical evaporator operating temperature. If the long-tube, vertical evaporator feed temperature was too low for as little as 20 minutes, scale started to form, but it redissolved in less than an hour after an increase in feed temperature resulted in the feed solution again being unsaturated at the boiling point.

The seeds were reactive to the extent that about 98 per cent of the potential $CaSO_4$ scale precipitated during a 35-second contact time.

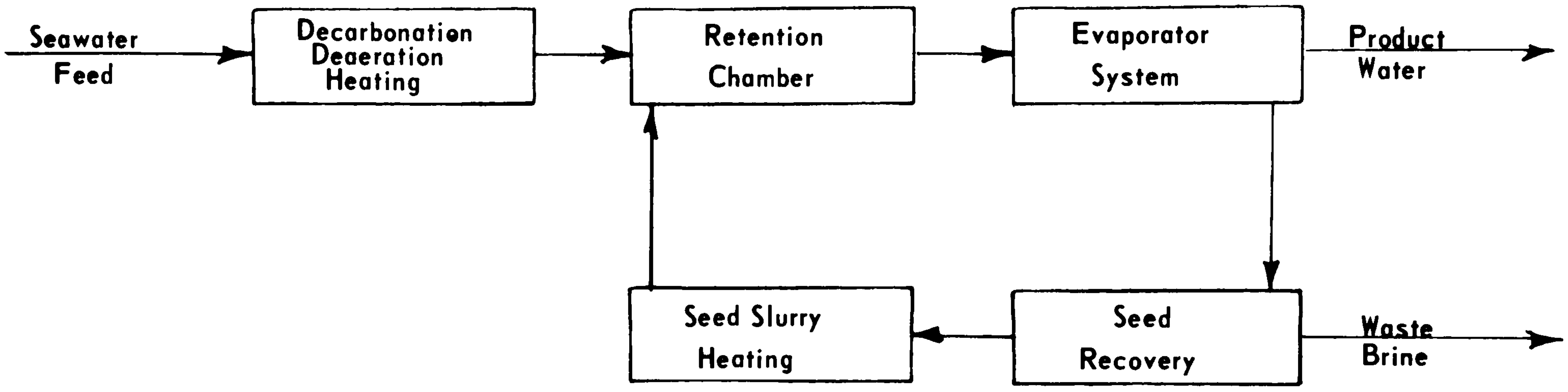
Scaling of the sea-water preheater occurred only in those sections where the sea-water temperature normally exceeded 300°F. Partway through the 495-hour run, the seed slurry was preheated separately to eliminate the possibility that preheater scaling might be aggravated by the seeds. The slurry-heater scaling rate was higher than that of the sea-water preheater, but was low enough that a full plant could be operated using two slurry heaters, one in service and the other being cleaned by flushing with warm sea water.

b. Process Adaptation to a Forward-Feed, Multiple-Effect, Long-Tube, Vertical-Evaporator System

The schematic diagram, Figure V-A7-1, illustrates the resulting flow pattern if the Badger process

FIG. V – A7 – 1

SCHEMATIC FLOW DIAGRAM OF BADGER SLURRY PROCESS



were added to a multiple-effect evaporator system. It will be helpful in visualizing the changes in concentrations and flow rates caused by the adaptation.

(1) $CaSO_4$ Solubility Path

Calcium sulfate solubility relationships are the heart of the process. As shown by Figure V-A4-5, normal sea water is saturated with respect to $CaSO_4$ (anhydrite) at temperatures above 235°F. The slow kinetics of anhydrite crystallization presumably allow further heating to slightly over 300°F where supersaturation is relieved by precipitation initiated by anhydrite seed crystals from the recirculated brine slurry. The first evaporator effect feed is unsaturated only to the extent that the anhydrite dissolution rate lags that slightly increased solubility because of the drop in temperature from the retention column to the first-effect boiling point.

As the brine slurry is cooled in passage through the evaporator system, anhydrite solubility increases because of the effect of both lowering temperature and increasing concentration factor. At an intermediate point, hydration of the dissolving $CaSO_4$ begins so that the last-effect brine-effluent concentration factor is limited instead by gypsum solubility at the brine temperature. Thus $CaSO_4$ solubility increases with brine passage from retention column to seed recovery, and conversely decreases with sea-water and seed-slurry heat-up to retention column temperature.

If the anhydrite-gypsum reversal proceeds completely with each temperature cycle of a given seed crystal, a calcium balance on the schematic diagram reveals that for scale-free plant operation, calcium entering in the sea-water feed equals calcium leaving in the saturated (no seeds) thickener brine overflow. So no $CaSO_4$ will be accumulated unless the last effect effluent is concentrated beyond gypsum saturation, and seeds may be lost by dissolution if the effluent is undersaturated. Lack of knowledge of the actual completeness of the anhydrite-gypsum transformation under a given set of conditions and for a given brine history hampers prediction of $CaSO_4$ gain or loss under this more probable incompletely reversed case.

(2) Seed Recovery

The Badger process requires the recovery of seed crystals for heating and recirculation to the retention column. This obviously requires a thickener, centrifuge, cyclone, or some other means of concentrating the effluent brine with respect to the solids contained. The importance of the degree to which the seeds are concentrated can hardly be over-emphasized. For a given retention-column seed concentration, the relative flow rates of sea-water feed and seed slurry are determined by the slurry-seed concentration. A lower slurry-seed concentration means a higher slurry flow rate, larger proportion of high concentration-factor brine being mixed with raw sea water, and thus a higher first-effect-feed dissolved-solids concentration. This, in turn, causes a higher boiling-point elevation in each effect.

For a given production rate and final-effect concentration factor, a higher first-effect concentration factor means a higher internal flow to be pumped through the evaporator system. The higher slurry flow rate requires a larger thickener, larger slurry pump, and larger slurry heaters for a given production rate.

The lower the slurry-seed concentration, the higher the heat capacity of the slurry and more potential scaling surface is required to heat it.

(3) Heat Transfer

Additional heat-transfer equipment is required to adapt the Badger process to a conventional multiple-effect, long-tube, vertical, distillation plant. The additional heat is required to superheat both the sea-water feed and seed slurry with respect to the first-effect boiling point. The sea water is heated from a few degrees below the first-effect vapor-head temperature, and the seed slurry heated from about the last-effect vapor-head temperature. The seeds do not completely eliminate high-temperature scaling, hence, this superheating merely transfers the risk of scaling from the first effect to the feed heaters. The same temperature steam supplying energy to the first effect may be used to superheat both the feed streams.

Since these additional feed heaters provide more heat-transfer surface through which energy may be put into the evaporator system, they are a means of increasing production provided the sea water and brine pumps can handle the higher flows required.

(4) Possible Operating Problems

The Freeport Conversion Plant has experienced considerable difficulty in handling suspended solids in the liquid streams. The silt incoming with the sea water has built up on the distribution plates in the evaporator water boxes and accelerated the problems caused by the flaking rust from the steel surfaces.

Sedimentation has been observed in many places of low velocity or in which the fluid has changed direction. Basket strainers have been added to the evaporator cone bottoms above the brine pumps and removable strainers have been considered. The silting problem has been so severe that the present settling basin has been repiped in an effort to remove as much as possible of the incoming sea-water solids.

A $CaSO_4$ slurry would be equally as troublesome, and would have the potential problems connected with recrystallization. Indeed, the hydration of either anhydrite or hemihydrate to gypsum (setting of plaster of paris) would, with the already existing solids, furnish an ideal mortar for the concrete.

Much care would have to be taken to prevent settling of the solids. Since a single pump failure would now shut down the train, the solids would be allowed to settle, particularly in the cone bottoms. Startup would be difficult, if not impossible. Sparing of all pumps would be desirable in a slurry system.

c. Heat- and Mass-Balance Calculation Procedure

(1) Process Temperatures

A heat- and mass-balance calculation procedure was developed for the adaptation of the Badger process to the Freeport Conversion Plant in order to determine the adequacy of the present equipment there. The same temperature distribution among effect vapor heads and 300-series condensers was used as was used in the 300°F revised process presented elsewhere in this report. Heat loss per effect was also taken as 0.3 per cent of total heat input from both steam condensation and brine superheat. Heat exchangers 208 through 211 were similarly replaced with flash tanks.

Some additional temperatures had to be specified. Sea water and seed slurry were both heated to 305°F by the same 316°F steam that went to the first effect. Condensate was routed to flash tank number one. This temperature was about 4°F above Effect I boiling point and should more than compensate for heat losses from the retention column. Feed was assumed to enter the Effect I at its boiling point. Thickener underflow was assumed to enter the slurry heater at 120°F, thus allowing about 2.5°F temperature drop in the thickener.

The same 75 - 25 Dow - Freeport product-water split was used in calculating exchanger 215.

(2) Badger Parameters

The Badger report specified a feed slurry concentration of about two grams of solids per 100 milliliters of slurry. These units proved unwieldly in subsequent calculations and so were converted to a weight-fraction basis. Using the concentration of the Badger feed as 1.43 times normal sea water, the two grams per 100 milliliters converted to a 0.0206 weight fraction at 305°F. This value was used throughout all seeding process calculations.

The limiting concentration in the last effect was taken as 3.5 times normal sea water(4).

(3) Steam Rate

It was not possible to utilize the full heat-transfer potential of Effect I in these balances. Normally, in calculating a hypothetical heat and material balance for the plant, the heat input of Effect I was determined, a production rate was estimated, and the required sea-water feed to achieve the desired Effect XII concentration was calculated. The balance was then calculated through the plant based strictly on the thermal properties of the streams until the actual effluent concentration was reached. As a first trial in the Badger adaptation, the Effect I over-all heat-transfer coefficient used was the one applied in the revised 300°F process (average of five actual operating coefficients). The resulting steam input to the effect plus the additional steam to the feed and slurry heaters yielded a production rate of over 790,000 pounds per hour (2.3 million gallons per day).

However, the flows and heat loads exceeded the capacity of all but two pumps, all but two of the 300-series condensers, the last four effects, and the present thickener. Time limitations did not permit incrementally reducing production and calculating new plant capital required for each increment.

Instead, the steam input which the present Effect I could handle was reduced by the amount required for the extra sea-water feed heater. Balances were then calculated for the cases of using the present 35-foot-diameter thickener and a 100-foot-diameter thickener, the largest the present site could accommodate. The difference in total steam input between the two cases reflected only the difference in the heat required by the respective slurry heaters.

(4) Procedure Steps

The first step in the calculation was to assume a net production rate. This could be based on an estimate of the steam economy times the steam input. The underflow-solids concentration which the thickener could produce at this production rate was then read off the generalized thickener calculation curve. (Calculation of this curve will be explained in the next section.) Use of a concentrated sea-water density chart and the handbook density of anhydrite enabled calculation of the underflow-solids weight fraction (Y_S) at 120°F.

To achieve the desired retention-column feed-solids weight fraction of 0.0206, the slurry flow rate had to be:

$$\frac{0.0206}{Y_S - 0.0206} \times \text{SWF}$$

The sea-water feed rate was calculated by the following equation:

$$\text{SWF} = \frac{3.5}{3.5 - 1.0} \text{ (Assumed net production + steam to deaerator)}$$

where 1.0 was the concentration of the sea-water feed (assumed to be normal sea water) and 3.5 was the last-effect effluent concentration. Both the slurry-feed rate (S) and sea-water feed rate (SWF) could then be calculated.

The concentration factor (CF) of the retention-column feed could be calculated by:

$$CF = \frac{3.5(1-Y_s)S + 1.0\ SWF}{(1-Y_s)S + SWF}$$

Solubility-product calculations showed that relief of $CaSO_4$ supersaturation in normal sea water at 305°F involved precipitation of only 2.0 per cent of the total dissolved solids in normal sea water. Thus the retention-column feed concentration factor could also be accurately used in determining the properties of the Effect I liquid feed.

For a typical balance the calculated heat capacity of the Effect I feed (including seeds) was 98 per cent of the brine heat capacity. The Effect XII effluent heat capacity was 96 per cent of the effluent-brine heat capacity. Hence, the heat capacity of the brine seed slurry throughout the system was taken as 97 per cent of the brine heat capacity at the same temperature.

The heat and mass balance could then be made on the evaporator system. If the desired last-effect effluent concentration was not attained with the desired accuracy, the assumed net production rate was correspondingly adjusted and the procedure repeated.

(5) Generalized Thickener Calculation

Ordinary procedure in plant design would be to specify a thickener underflow-solids concentration and then calculate the thickener dimensions required. However, in this case, the diameter of the thickener was given and the expected performance had to be calculated. The performance would vary with the volume flow to the thickener and thus with the production rate.

A generalized plot of thickener underflow-solids concentration as a function of thickener area was prepared with net production rate as an additional parameter to be specified. The Kynch theory, based on the determination of the settling rate and capacity-limiting zone from a single batch-settling test, was the basis of the calculations(38).

Two sets of batch-settling test curves are presented in the Badger report, one for the long-tube, vertical, evaporator feed and one for the thickener underflow. The feed data was used by Badger to predict that the 35-foot Freeport thickener would be adequate for a two-million-gallon-per-day output. The settling velocity at free-settling conditions was calculated. It averaged 0.96 inches per minute and corresponded to an average Stokes diameter of 17 microns.

The Badger pilot-plant clarifier was larger than needed and required underflow recycle to avoid over-thickening and an excessively low flow rate through the slurry heater. The underflow batch-settling test was used by Badger to predict that the 14-foot deep Freeport thickener could achieve the ultimate settled density of 70 grams solids per 100 milliliters. Initial underflow-solids concentration in the settling tests was in the range 17-22 grams solids per 100 milliliters.

It was unfortunate that samples of the actual thickener feed were not subjected to batch-settling tests because of the widely varying settling rates between the feed and thickener underflow samples. For example, application of the Kynch method to the 17 grams solids per 100 milliliters underflow sample showed that at a production rate of 1,554,000 gallons per day, the Freeport thickener could further concentrate to only 18.5 grams solids per 100 milliliters. At a two million-gallon-per-day rate, the concentration would be even less.

One reason for the discrepancy in the calculated performance of the Freeport thickener could be that the Badger calculation apparently was based on the settling rate in the upper clarification zone, whereas, when the slurry approached hindered settling conditions, the actual capacity-limiting zone was revealed in the underflow settling test calculations. These latter calculations and the generalized thickener plot will be used in the heat and material balances presented in this report.

d. Results of Badger Process Adaptation to Freeport Conversion Plant

Figure V-A7-2 illustrates the process flow lines for the Badger process adaptation to the Freeport Conversion Plant. Alternate slurry heaters are provided for the higher temperature heating of the seed slurry. A large excess of cooling water from the 312 surface condenser would always be available for flushing out the off-stream slurry heater.

(1) Present Thickener Case

A summary of the heat- and material-balance results for the adaptation using the present Freeport thickener is shown below.

Sea-water feed rate - 896,000 lb/hr
Slurry rate - 141,700 lb/hr
Including 18 gms seeds per 100 ml

85 psia steam input:

300 SWF heater	9,848 lb/hr
Effect I	46,499 lb/hr
Slurry heater	23,119 lb/hr
	79,466 lb/hr

Net production: 640,000 lb/hr
Gross production: 719,466 lb/hr = 2,069,000 gpd

Steam economy - 8.05 $\frac{\text{lb net water}}{\text{lb steam}}$

FIG. V-A7-2
BADGER 300 °F SEEDING PROCESS
Thickener Seed Recovery

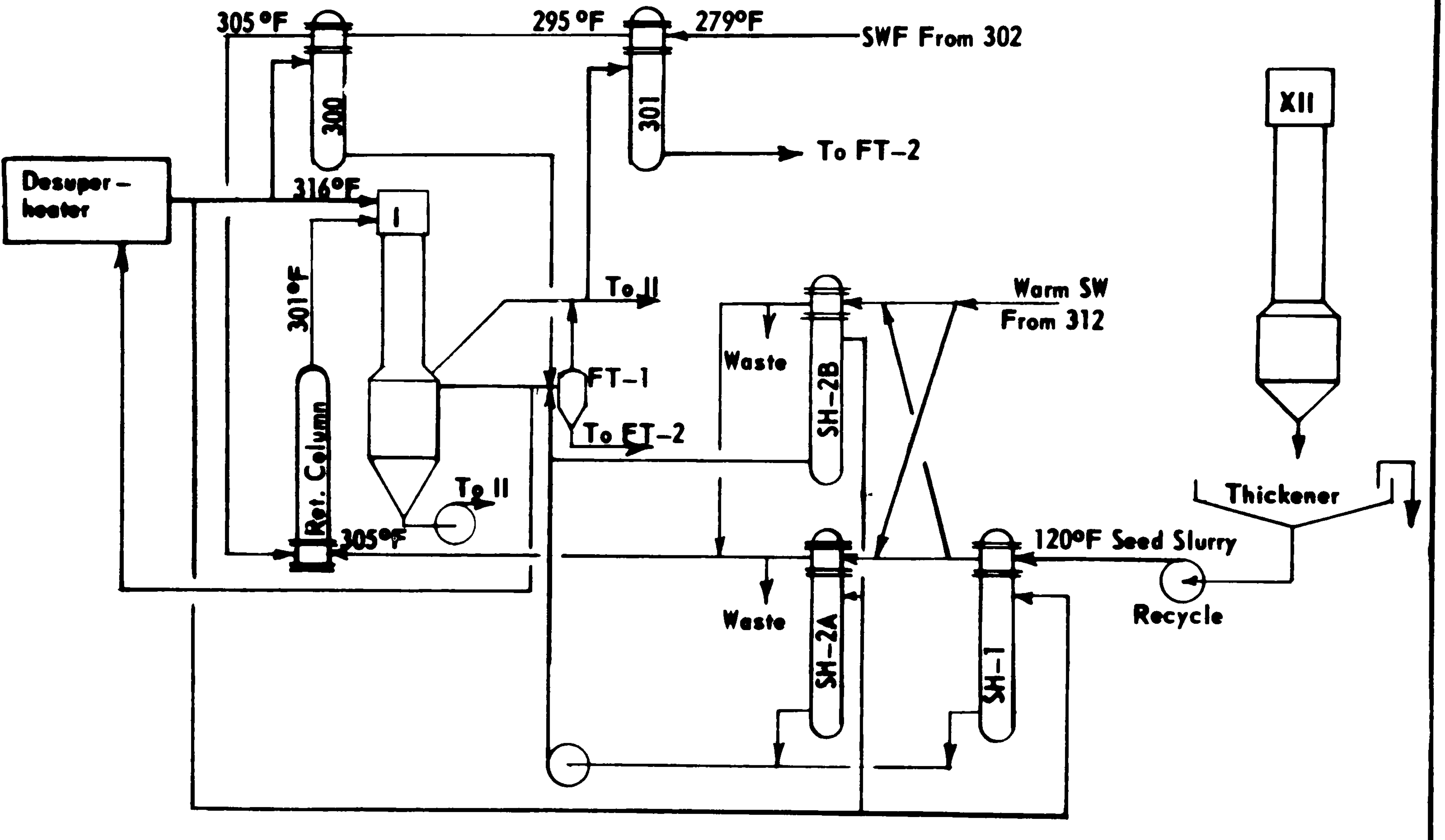


Table V-A-7-I lists the equipment changes needed to accommodate the balance values. The retention column was designed for a one-minute contact time. The cost of the present thickener was deducted from plant capital investment in 1962 by Stearns-Roger Corporation, the plant operating company, and also is not included in the estimate of present plant capital earlier in this report. Costs given here for modified or replacement equipment is compared with the purchased cost of present plant equipment in Table V-A-7-I. The additional equipment costs are the fabricated or purchased costs.

(2) New 100-Foot Thickener Case

Listed below are the results of the heat and material balance for the use of a 100-foot-diameter thickener in the adaptation of the Badger process to the Freeport Conversion Plant.

Sea-water feed rate - 806,400 lb/hr
Slurry rate - 55,700 lb/hr
Including 43 gms seeds per 100 ml

85 psia steam input:

300 SWF heater	8,863	lb/hr
Effect I	47,484	lb/hr
Slurry heater	7,716	lb/hr
	64,063	lb/hr

Net production: 576,000 lb/hr
Gross production: 640,063 lb/hr = 1,841,000 gpd

Steam economy - $8.99\ \frac{\text{lb net water}}{\text{lb steam}}$

Table V-A-7-II lists the equipment changes needed to accommodate the balance values. Costs are on the same basis as Table V-A-7-I.

TABLE V-A-7-1

EQUIPMENT CHANGES USING PRESENT THICKENER IN BADGER SEED SLURRY ADAPTATION

	Equipment Cost	
Modified	Present	Seed Slurry
Pumps, P-1 and P-2	$ 16,310	$ 18,760
P-3	1,782	2,132
P-44	1,118	1,418
P-51	1,603	1,903
Effect IX, Add 12 tubes	28,490	29,040
Effect X, Add 78 tubes	28,243	32,073
302 Condenser, Add 78 tubes, tube out	5,682	7,492
303 Condenser, Add 69 tubes, tube out	6,615	8,215
307 Condenser, Add 29 tubes, tube out	7,330	8,000
Total	$ 97,173	$109,033
Replacement		
304 Condenser, 31-in. shell tubed out	7,794	9,095
308 Condenser, 31-in. shell tubed out	7,830	9,095
309 Condenser, 31-in. shell tubed out	6,480	9,095
310 Condenser, 31-in. shell tubed out	7,665	9,095
311 Condenser, 31-in. shell tubed out	7,006	9,095
312 Surface Condenser, Change to 28-ft tubes, same shell ID and tube count	18,685	30,200
Effect XI, 70-in. ID, 702 tubes (24-ft)	34,800	39,920
Effect XII, 83-in. ID, 995 tubes (24-ft)	35,000	55,100
Pumps and Motors, all except those modified	39,470	40,748
Total	$164,730	$211,443
Additional		
35-ft Thickener	0	17,000
Slurry Recycle Pump with 25 Hp Motor	0	1,630
3 Slurry Heaters, 17-1/4-in. shell; 3/4-in., 18-BWG, Al-Br 12-ft tubes at $3,250	0	9,750
SWF Preheater, same as 301 Condenser, 28-in. shell	0	7,830
Retention Column 4-ft diameter x 22-ft	0	3,770
Total	0	$ 39,980
Total Cost of Equipment	$261,903	$360,456

TABLE V-A-7-11

EQUIPMENT CHANGES USING 100-ft DIAMETER THICKENER IN BADGER SEED SLURRY ADAPTATION

	Equipment Cost	
Modified	Present	Seed Slurry
Pumps, P-1 and P-2	$ 16,310	$ 18,760
P-3	1,782	2,132
P-44	1,118	1,418
P-51	1,603	1,903
Effect X, Add 40 tubes	28,243	30,203
Effect XI, Add 4 tubes	34,800	35,000
303 Condenser, Add 69 tubes, tube out	6,615	8,215
Total	$ 90,471	$ 97,631
Replacement		
304 Condenser, 31-in. shell tubed out	7,794	9,095
308 Condenser, 31-in. shell tubed out	7,830	9,095
309 Condenser, 31-in. shell tubed out	6,480	9,095
310 Condenser, 31-in. shell tubed out	7,665	9,095
311 Condenser, 31-in. shell tubed out	7,005	9,095
312 Surface Condenser, Present ID and tube count 22-ft tubes	18,685	24,475
Effect XII, 76-in. ID, 825 tubes (24-ft)	35,000	50,300
Pumps and Motors, all except those modified	39,470	39,270
Total	$129,929	$159,520
Additional		
100-ft Thickener, Earthfilled Sides	0	50,000
Slurry Recycle Pump with 15 Hp Motor	0	1,340
3 Slurry Heaters, 12-in. shell; 3/4-in., 18-BWG, Al-Br 10-ft tubes at $2,310	0	6,930
SWF Preheater, same as 301 Condenser	0	7,830
Retention Column 4-ft diameter x 18-1/2-ft	0	3,400
Total	0	$ 69,500
Total Cost of Equipment	$220,400	$326,651

e. Badger Process Adaptation Using High-Temperature Seed Recovery

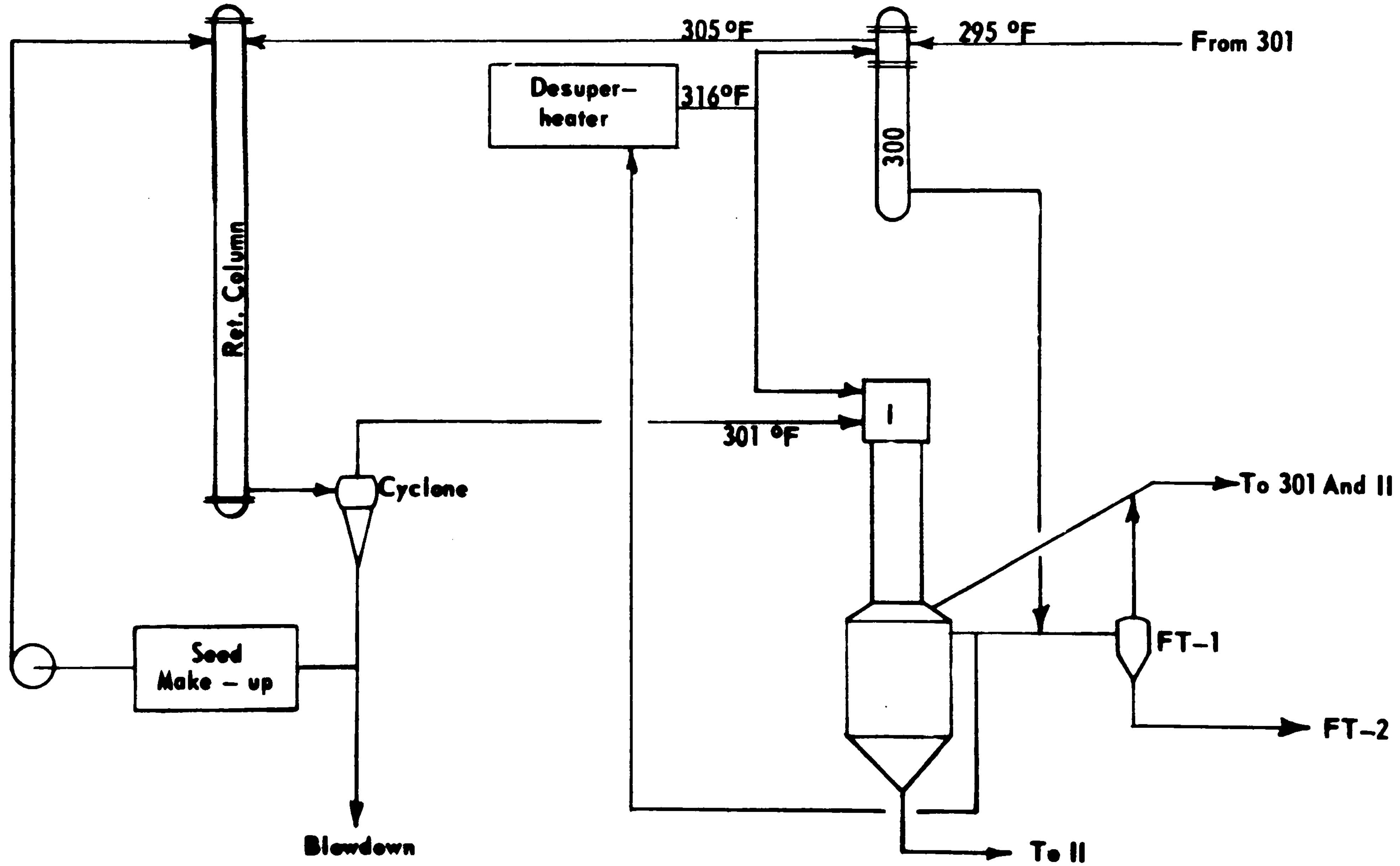
Removal of the larger seed crystals by settling out in the retention column was suggested in the Badger report. Recovery of all seeds immediately after use in the retention column has several advantages over thickener seed recovery at a lower temperature. A higher steam economy, less potential scaling surface, and reduced capital cost would result from the elimination of the slurry heaters. None of the potential operating problems attendant to feed-slurry passage through the effects could materialize. With these points in mind, the Badger process using high-temperature, pre-Effect-I, hydraulic-cyclone seed recovery was hypothetically adopted to the Freeport Conversion Plant as shown in Figure V-A7-3.

Performance of the seed-recovery equipment is critical here as it was in the thickener adaptation, and cyclone performance must be specified before a heat and material balance can be calculated. Seed recovery could fall into one of three areas.

If the weight of seeds removed in the cyclone underflow exactly equals the weight fed to the retention column, the Effect-I feed must contain the same Ca and SO_4 content as the sea-water feed. The net effect would then be simply the precipitation of $CaSO_4$ equivalent to that required to relieve the supersaturation at retention-column temperature. The solubility product of $CaSO_4$ in normal sea water at 305°F is 43×10^{-4} (weight per cent squared) according to Figure V-A4-3. Using this solubility product, the retention-column-feed seed weight fraction of 0.0206, and assuming one-fourth of the cyclone feed leaves it as underflow, the cyclone efficiency for this case would be 97.5 per cent.

If the cyclone could not remove this percentage of seeds, the case exists in which seed make-up would be required. The plant would not be operated this way continuously, but provision should be made in any process design to add $CaSO_4$ for start-up purposes.

FIG. V – A7 – 3
BADGER 300 °F SEEDING PROCESS
Cyclone Seed Re covery



If the cyclone removed more seeds than specified in the first case, part of the underflow stream must be blown down to maintain a constant retention-column feed concentration. This case was the most desirable because the total $CaSO_4$ content at the Effect-I feed would be less than the sea-water feed and the limit to which it could be concentrated without exceeding gypsum solubility would be extended. Adding to the assumptions made in calculating the first case, the assumption that the cyclone operates with 99 per cent efficiency, all flows and seed concentration to and from the retention column and the cyclone may be calculated by solving six simultaneous equations. The results are shown in Figure V-A7-4. All flows are in terms of the sea-water feed rate and all concentrations are in seed weight fractions.

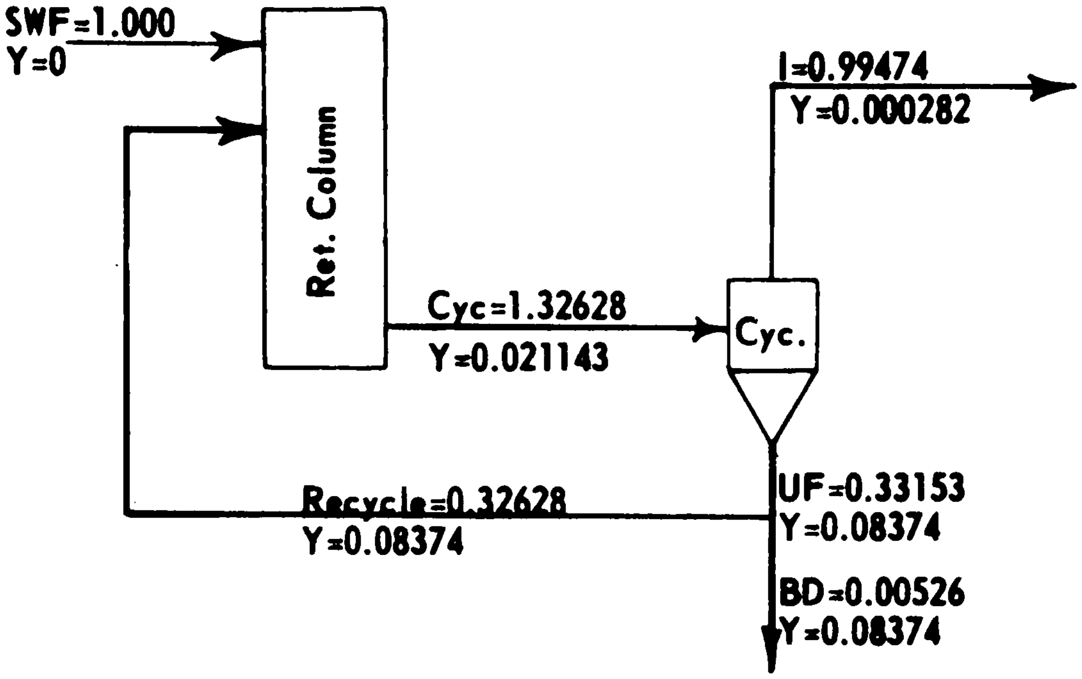
The limiting concentration factor in Effect XII for all three cases is shown below. Since these calculations were an extension by Dow of the Badger process, the more conservative 2.9 limiting concentration factor presented by Dow in Figure V-A4-5 for normal sea water was used as the base. The product of Ca and SO_4 weight percentages in Effect-I feed includes both liquid and solids in the slurry.

Cyclone Efficiency, Fraction Solid Recovery	Gypsum Potential, $(Ca)(SO_4)$ (weight per cent)^2	Limiting Effect-XII Concentration Factor - from Figure V-A4-4
0.9745	0.011027	2.9
<0.9745	>0.011027	<2.9
0.9900	0.006679	3.6
1.00	0.00430	4.5

The flow and concentration values calculated for the 99-per-cent-efficient cyclone were used in preparing a heat and material balance for cyclone use in the Badger process adaptation. The limiting Effect-XII concentration factor was taken as 3.6. It was assumed the seed slurry did not cool enough in passage through the cyclone to require a slurry heater. The same temperature distributions and heat-loss factor were used as were used in the revised 300°F balance presented

FIG. V-A7 - 4

BADGER PROCESS-RETENTION AND SEPARATION



SWF = Seawater Feed
UF = Cyclone Underflow, Fraction Of SWF
BD = Brine Discharge, Fraction Of SWF
Cyc. = Feed Cyclone, Fraction Of SWF
Y = Concentration, Weight Fraction

elsewhere in this report. Heat exchangers 208 through 211 were replaced with flash tanks.

The results of the heat and material balance were:

Sea-water feed rate - 744,700 lb/hr
Cyclone underflow at 8.4 gms seeds per 100 ml
Included recycled slurry - 243,000 lb/hr
Blowdown - 3,900

85 psia steam input:

300 SWF heater	8,185	lb/hr
Effect I	48,162	lb/hr
	56,347	lb/hr

Net production:	535,000	lb/hr
Gross production:	591,347	lb/hr =
	1,701,000	gpd

Steam economy - $9.49 \ \frac{\text{lb net water}}{\text{lb steam}}$

Table V-A-7-III lists the equipment changes needed to accommodate the balance values. Estimates were obtained on both centrifuges and hydraulic cyclones as means of seed recovery before Effect I. The cyclone alternative was cheaper by a factor of twenty, and the cost estimate given for it is based on a Dorr-Oliver Pipeline Solids Separator or its equivalent.

TABLE V-A-7-III

EQUIPMENT CHANGES USING CYCLONE SEED RECOVERY IN BADGER SEED SLURRY ADAPTATION

	Equipment Cost	
Modified	Present	Seed Slurry
Pumps, P-1 and P-2	$ 16,310	$ 18,760
P-3	1,782	1,952
P-44	1,118	1,418
P-51	1,603	1,903
303 Condenser, Add 69 tubes, tube out	6,615	8,215
Total	$ 27,428	$ 32,248
Replacement		
308 Condenser, 31-in. shell tubed out	7,830	9,095
309 Condenser, 31-in. shell tubed out	6,480	9,095
310 Condenser, 31-in. shell tubed out	7,665	9,095
311 Condenser, 31-in. shell tubed out	7,005	9,095
312 Surface Condenser, 20-ft tubes, same shell ID and tube count	18,685	22,515
Effect XII, 70-in. ID, 705 tubes (24-ft)	35,000	39,920
Pumps and Motors, all except those modified	39,470	39,000
Total	$122,135	$137,815
Additional		
Slurry Recycle Pump with 40 Hp Motor	0	2,370
SWF Preheater, same as 301 Condenser	0	7,830
Retention Column, 4-ft diameter x 22-ft high	0	3,770
2 Cyclones 24-in. diameter at $8,000	0	16,000
Total	0	$ 29,970
Total Cost of Equipment	$149,563	$200,033

f. Conclusions and Recommendations

The Badger 300°F seeding process should permit 300°F operation of the first effect of a long-tube, vertical, distillation plant. However, the pilot-plant report indicates scaling is by no means eliminated. A lessened amount of scale is possible in the feed and slurry preheaters.

Summarizing the adaptation balances:

Seed Recovery	Gross Daily Production, mm gal	Steam Economy, lb net water / lb steam	Additional Capital Req'd, Purchased Cost
Present thickener	2.069	8.05	$ 98,553
New 100-foot-diameter thickener	1.841	8.99	106,251
Two new hydraulic cyclones	1.701	9.49	54,070

The only rate equation which limited the three Badger-process-adaptation balances pertained to the performance of the seed recovery equipment. The steam economy calculated should then be representative of the process adaptation having the given thickener or cyclone-underflow seed concentration, and should be independent of heat-transfer rate considerations. As expected, the case with the lower thickener-slurry concentration had the poorest steam economy, and the cyclone case, requiring no slurry reheating, had the best. Since steam cost is normally over 30 per cent of the total water cost, this is a significant advantage. The steam economy of all three cases could be improved incrementally if one were willing to risk less superheating of the retention-column feed streams with respect to the Effect-I boiling point.

From the standpoint of the additional capital required, the cyclone case also appears to be the most economical. Capital cost estimates made here should be compared only among the three adaptations, and caution exercised in any comparison to other plants of the same production rate. This is because it was not possible to utilize the maximum heat-transfer capacity of all the effects as explained previously. Economics of the adaptations would show up more favorably in plants designed specifically for them.

Some additional technical information would be helpful to the future development of the seeding process.

Batch-settling test data on actual Effect-XII-brine seed-slurry samples is needed. Concentration of this slurry beyond 43 grams per 100 milliliters would make possible an increase in steam economy for the thickener adaptation. Experimental experience in pumping and heating $CaSO_4$ slurries in the concentration range 40-70 grams per 100 milliliters is desirable.

Pilot-plant work on hydraulic-cyclone performance under the desired conditions prior to Effect I would be very valuable. An evaporator system would not be needed for this investigation. However, the sea water should be heated without scale to 305°F.

B. Product Water

1. Estimate the effects of product water on materials of construction and expected corrosion of metallic systems. Examine test spools and plant piping. Determine Langelier Index of product water and chemical requirements for water balancing.

   a. General conclusions of the study of the product water are:

      (1) The water is considerably more corrosive than either raw Freeport well water or than chlorinated Freeport well water (refer to Table V-B-1-I).

      (2) Its normally corrosive nature is due to its lack of scale-forming ability. This is to be expected of any very pure water. Its normal corrosiveness is enhanced by the presence of free CO_2 during irregular intervals.

      (3) Treatment of the product water at the Freeport Conversion Plant with ten parts per million $CaCl_2$, plus ten parts per million Na_2CO_3 has been beneficial. This has decreased the rate of corrosion of plain steel in the water to about one-half of that which would exist without the treatment.

      (4) Blending the converted water with Freeport well water in the approximate ratio 25:65 respectively, has produced a water that is only slightly more corrosive than chlorinated Freeport well water.

   b. Effects of Product Water on Materials of Construction

      The corrosion rates of carbon steel (SAE 1010) in the various waters involved were measured by both direct weight loss and by resistance corrosometer probes. The direct weight loss method involved the installation of 3/4-inch by three-inch weighed coupons of carbon steel mounted on Micarta-rod holders, directly into the pipeline involved. The coupons were always installed edge-on to the flow. The corrosometer probes were also carbon steel of the flat strip type. They were obtained from the Magna Corporation, and were monitored with a Magna "Crest" Corrosometer.

Table V-B-1-I shows the rates at which carbon steel corrodes in the various waters with which the Freeport Conversion Plant is involved. The corrosion rates are expressed in mils penetration per year, assuming a uniform attack over the entire exposed surface. The values obtained by direct weight loss are considered to be more reliable than those obtained with the corrosometer.

The rate and identity of the treatment chemicals added to the product water sent to Freeport were varied over four to six hour periods. During these periods the corrosion rate inside the product-water line was monitored with the corrosometer. The results are shown in Table V-B-1-II. The results are not considered to be very meaningful, since the period of observation was not of sufficient duration.

Examination of the coupons exposed in the product-water line to Freeport revealed that the corrosion product is entirely magnetite, Fe_3O_4. Under most conditions the physical form of the magnetite is a tightly adherent, impervious film, which to a great extent protects the base metal. Under the conditions existing in the product-water line, the magnetite was a loose, porous sponge of very finely divided particles. Since Fe_3O_4 is relatively electrically conductive, the spongy mass apparently has afforded a very large cathodic area in close electrical contact with the corroding anodic areas. This is interesting, not only from an academic standpoint, but it also offers a clue to a possible solution to the corrosion problem of the product water. This would be to completely aerate a side-stream of the product water on an experimental basis. The presence of a sufficient supply of dissolved O_2 might actually reduce the corrosion rate of steel by altering the nature of the corrosion product.

TABLE V-B-1-I

CORROSION RATES OF PLAIN STEEL IN VARIOUS WATERS RELATING TO THE FREEPORT CONVERSION PLANT

Water Identity and Location	Penetration Rate in mils per year	
	By Corrosometer	By Weight Loss
Converted Water in Dow Pipeline	20.6 (32)	5.5 (14)
Converted Water in Freeport Pipeline	20.6 (17)	13.0 (43) 9.5 (14)
Raw No. 4 Well Water at Wellhead	0.67 (15)	4.42 (43) 1.23 (11) 1.41 (14)
Chlorinated No. 4 Well Water in Main	3.38 (4) 3.08 (7)	4.47 (43)
Chlorinated Blended Water in Main (Contains about 30 per cent to 35 per cent Converted Water)	5.45 (32) 3.5 (14)	5.05 (43) 4.56 (14)

NOTE: Figures in parentheses are the periods of exposure in days.

TABLE V-B-1-II

RESULTS OF VARYING THE "TREATMENT" CHEMICALS TO THE PRODUCT WATER

Treatment	Mils/year penetration by corrosometer probe
1. Add 10 ppm $CaCl_2$ plus 10 ppm Na_2CO_3 (normal treatment)	20.6
2. Add nothing	31
3. Add 20 ppm $CaCl_2$ plus 20 ppm Na_2CO_3	31
4. Add 10 ppm Na_2CO_3 only	28
5. Add 20 ppm $CaCO_3$ powder (325 mesh ground limestone)	47

NOTE: The periods of trial addition of treatment chemicals, (except for the normal treatment) was four to six hours. This time is now considered much too short for meaningful results.

c. Langelier Index of Product Water

Prior to the addition of the ten parts per million $CaCl_2$ and ten parts per million Na_2CO_3 to the product water to Freeport, a typical analysis of the latter was:

Total Dissolved Solids = 20 parts per million
Total Hardness = 3.0 parts per million $CaCO_3$
Total Alkalinity = 4.0 parts per million $CaCO_3$
pH = 6.8

This water has a Langelier Index of -3.85, indicating a water of a corrosive nature, since the theoretical pH necessary to cause the water to be just saturated with $CaCO_3$ (saturation pH) is 10.65.

The addition of ten parts per million $CaCl_2$ and ten parts per million Na_2CO_3 to the product water forms approximately ten parts per million $CaCO_3$. This has resulted in a water whose actual pH has varied from 6.8 to 9.5. Consequently its Langelier Index has varied from -2.7 to -0.034. This range in pH is the result of variations in the relative rates at which the two treatment chemicals are fed to the product water, and to the irregular occurrence of free CO_2 in the water

The use of the Langelier Index(17),(3) is an arbitrary but useful way of quantitatively rating a water as to its relative corrosive or scaling properties. It is numerically equal to the difference between the actual pH of the water and the "saturation" pH. The latter, in turn, is the theoretical pH which would have to prevail in the water, in order for it to be exactly saturated with respect to $CaCO_3$. If the index is positive, $CaCO_3$ will deposit from solution, and the water is said to be "scale-forming". If the index is negative, the water should dissolve scales already deposited, and the water is termed corrosive or "aggressive". Thus, water from No. 4 well in Freeport has a Langelier Index of +0.4, corresponding to slightly scale-forming. The index of the blend of Freeport well water with converted product water in the ratio currently being used results in an index of about -0.1.

d. Chemical Requirement for Producing a Balanced Water

A balanced water, in the Langelier sense, will be produced if the addition of $CaCl_2$ is increased from ten parts per million to 46 parts per million, the addition of Na_2CO_3 is increased from ten parts per million to 43 parts per million, and four parts per million $Ca(OH)_2$ is added. A combination of these changes should produce a water with a Langelier Index of about zero, with a pH of between 8.5 and 9.0. The new rates assume 4.0 parts per million $CaCO_3$ and 4.0 parts per million free CO_2 already present in the product water prior to adding the treatment chemicals.

The above changes can be effected with little or no additional equipment required. This is not necessarily the method resulting in the lowest over-all operating cost.

B. Product Water

2. Develop necessary process changes to produce a chemically balanced water. Estimate the effects of mixing product water with Freeport city water. Recommend a water treatment system, the capital requirements, and operating cost.

a. Recommendations

Final recommendations of a water treatment system cannot be made at this time, as the separate effects of several different trial changes must first be observed. The methods must then be compared for effectiveness and cost before the most advantageous one is selected.

The following program of trial operation is recommended. The steps should be taken consecutively in the order given.

(1) Alter the rates of addition of the treatment chemicals, as recommended in paragraph V-B-1-d, i.e., inject 46 parts per million $CaCl_2$, 43 parts per million Na_2CO_3, and four parts per million $Ca(OH)_2$. The $Ca(OH)_2$ can be added by mixing in with the $CaCl_2$ in the proper ratio. These conditions should be held constant for a period of about one week, while the corrosion rate is being monitored with corrosometer probes in the product-water line and in the blended-water line.

(2) Discontinue Step 1. Add 45 parts per million of precipitated $CaCO_3$ to the product-water influent to the storage tank, and monitor the pH values as before. The grade of $CaCO_3$ used should be one in which the maximum particle size is less than ten microns. "Pigment grade" precipitated calcium carbonate is recommended. (Note: The injection of ten parts per million $CaCO_3$ consisting of 325-mesh ground limestone has already been attempted without success, apparently because the material was too coarse to completely dissolve during its residence time in the storage tank.) The pH of the product-water effluent from the storage tank should be about 8.5. If the latter value is not attained, then $Ca(OH)_2$ slurry should be injected into the product water leaving the tank to

maintain a pH of 9.0. The expected $Ca(OH)_2$ requirement is less than four parts per million. Monitor the corrosion rates as before.

(3) Discontinue Step 2. Add enough lime water to the product-water influent to the product-water storage tank, to produce a pH of 9.5 in the product-water line to Freeport. Monitor the corrosion rates in the product-water line to Freeport, and in the blended-water line in Freeport as before.

(4) Discontinue Step 3. Add ten parts per million sodium tripolyphosphate to the product-water influent to the storage tank, plus sufficient $Ca(OH)_2$ slurry to maintain the product-water effluent from the storage tank at a pH of between 9.0 and 9.5. Monitor corrosion rates as before.

Each of the above sets of conditions should each be maintained for approximately one week, during which the corrosion rates are monitored with a corrosometer.

b. Discussion

In Step 1 and Step 2 of the four sets of experimental conditions recommended above, the objective is to produce a product water containing about 47 parts per million $CaCO_3$ in solution, and only enough dissolved, free CO_2 to be in equilibrium with normal air. Under these conditions the actual pH will be about 8.4 and will be equal to the saturation pH. The Langelier Index will therefore be zero. By adjusting the pH upward slightly, a positive index can be attained.

There is no uncertainty connected with obtaining a Langelier Index of zero by the conditions of Step 1. The disadvantages are the chemical cost (approximately \$0.03 per 1000 gallons of product water) and the fact that approximately two parts per million of dissolved solids are added to the product water for each one part per million of dissolved $CaCO_3$ formed:

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\ NaCl$$

The chemical cost of Step 2 is only \$0.014 per 1000 gallons of product water, and no dissolved solids other than $CaCO_3$ are added. However, it is not certain that commercially obtainable grades of $CaCO_3$ will have a sufficiently small particle size for complete solution to occur during the residence in the product-water storage tank and product-water pipeline.

In Step 3, the addition of $Ca(OH)_2$ to the product water to maintain 9.0 to 9.5 pH reduces the dissolved, free CO_2 content to a negligible value. The corrosion rate obtained under this condition is used as a basis value to determine the effectiveness of adding a corrosion inhibitor in Step 4.

Phosphates are known to be anodic corrosion inhibitors. Their addition to the product water should inhibit the corrosion reactions appreciably. The cost of the sodium phosphate at $0.10 per pound will be $0.0083 per 1000 gallons of product water. The cost of the lime would be approximately $0.0005 per 1000 gallons of product water. The disadvantage is that sodium phosphate does not normally occur in most drinking waters of natural origin, and from a psychological viewpoint, something "foreign" will have been added. A further disadvantage of adding sodium phosphate is that as an anodic inhibitor it will increase the likelihood of pitting at the anodic areas, even though the average over-all rate of corrosion would be reduced.

Two corrosometer probes, at about $70 each, will be required for the entire experimental program outlined above. The equipment necessary for the experimental addition of treatment chemicals is already on hand at the Freeport Conversion Plant. Should any one of the above methods be adopted on a permanent basis, the equipment cost will be small. For the method of Step 1, which requires the most equipment of the three, $1200 has been estimated as the installed cost of: two 110-gallon drums, one 55-gallon drum, three metering pumps, three rotameters, and one "Lightnin'" mixer.

This estimate is only approximate and assumes the existing equipment for adding the treatment chemicals is not adequate in size for the permanent installation. A detailed cost estimate should be made after the selection of the most effective process. It is entirely possible that no additional equipment will be required if the method of Step 4 is used.

If the method described in Step 1 is found to satisfactorily reduce the corrosiveness of the product water, and, if the method described in Step 2 is found to be unworkable because of low dissolving rates of $CaCO_3$, then the following method of obtaining a product water saturated with $CaCO_3$ should be considered. The latter would reduce the cost of the chemicals of the method of Step 1, but would require considerably more additional capital.

The exhaust from vacuum pump VP-1 contains sufficient CO_2 (a CO_2 partial pressure of 0.7 atmosphere) to saturate the product water to Freeport with $CaCO_3$ if $Ca(OH)_2$ is also added to the product water in the correct amount. A side stream, say two to three gallons per minute, of product water is bled off the main stream of product-water influent to the storage tank. Approximately nine parts per million (based on total product-water rate to Freeport) of $Ca(OH)_2$ is injected into this side stream. The side stream is now sprayed into an unpacked tower (about two-feet diameter by about seven-feet high), countercurrent to the upward flow of gases from the vacuum-pump exhaust. The effluent from the tower, containing all the Ca in soluble form, is now reinjected into the product-water line to the product storage tank at a point slightly downstream from the initial point of withdrawal. At the point of reinjection, an additional 27 parts per million (based on total product-water rate to Freeport) of $Ca(OH)_2$ is injected directly into the product-water line.

Calculations show that with a partial pressure of CO_2 of 0.7 atmosphere in the vacuum-pump exhaust, the composition of the effluent from the small carbonating tower will be approximately:

Ca = 0.98×10^{-2} gram mols per liter
HCO_3^- = 1.95×10^{-2} gram mols per liter
free CO_2 = 2.2×10^{-2} gram mols per liter
pH = 6.3

The equation describing approximately the reaction occurring in the carbonating tower is, then:

$$4\ CO_2\ (g) + Ca(OH)_2 \longrightarrow Ca(HCO_3)_2 + 2\ CO_2\ (aq)$$

Inside the product-water line, at the point of reinjection, the reaction would be:

$$2\ CO_2\ (aq) + Ca(HCO_3)_2 + 3\ Ca(OH)_2 \longrightarrow 4\ CaCO_3 + 4\ H_2O$$

By making slight adjustments in the flow of $Ca(OH)_2$ injected directly into the product-water line and the flow of $Ca(OH)_2$ to the carbonating tower, the Langelier Index of the product water can be varied over a wide range of values.

The total cost for chemicals for this method would be the cost of the lime, and would amount to approximately $0.0034 per 1000 gallons product water, as compared to about $0.031 per 1000 gallons for the method of Step 1. The capital cost for the method just described is estimated to be about $2500. Under existing water rates to Freeport, this capital addition could be paid out in about 15 months by the saving in chemical costs.

SECTION VI. ECONOMICS OF DESALINATION PLANTS

Economic evaluation of the present and revised operations of the Freeport Conversion Plant and a normalized long-tube, vertical, distillation plant is based on criteria set forth by Bechtel Corporation(5). All cases are evaluated for 330 operating days per year.

A. Present Plant Economics

The principal items of equipment are estimated at 1964 prices and the equipment costs, Table VI-A-I, are installed costs. All equipment used in the present operation is included for the determination of the capital cost. Erection and assembly cost is calculated as 20 per cent of the cost for the principal items of equipment and includes site development, concrete work, overhead crane, painting, and insulation. Engineering and start-up costs used were given for the demonstration plant by Bechtel. The capital cost is $1.60 per gallon of daily capacity.

The chemical consumption at a production of one million gallons per day is 40 pounds per day of $CaCl_2$, 40 pounds per day of Na_2CO_3, 1200 pounds per day of H_2SO_4, and 320 pounds per day of NaOH.

The operating costs are computed from plant data for steam, chemicals, and electric power consumption. Prices for these items were obtained from plant records. The labor cost was obtained from Stearns-Roger's annual report(48) and was based on present operating procedures. The cost of water, Table VI-A-II, was computed from annual operating costs and annual production and was found to be $1.29 per thousand gallons of product water.

TABLE VI-A-I

CAPITAL COST FOR THE PRESENT PLANT

Principal Items of Equipment	
1. Evaporator Effects	$ 608,396
2. 300-Series Exchangers	103,233
3. 200-Series Exchangers	91,124
4. 312 Condenser	24,215
5. Deaerator	19,822
6. Flash Tanks	12,652
7. Pumps	78,368
8. Vacuum and Air Compressors	14,898
9. Acid and Caustic Systems	5,630
10. Sea-Water Intake	49,317
11. Desuperheater	2,080
12. Electrical and Piping	140,400
13. Product Storage Tank	3,500
TOTAL PRINCIPAL ITEMS OF EQUIPMENT	$1,153,635
14. Erection and Assembly	163,342
15. Instruments	52,629
16. Operations Buildings	42,800
17. Land	3,000
18. Engineering	167,000
19. Start-Up	22,000
TOTAL CAPITAL COST	$1,604,406
CAPITAL COST PER GALLON OF DAILY CAPACITY	$1.60

TABLE VI-A-II

COST OF WATER
PRESENT PLANT OPERATION

Plant Data

Plant Capacity, million gpd	1
Annual Production, millions of gallons	330
Economy Ratio, gross lb water/lb steam	10.95
Capital Cost, dollars	1,604,406

Direct Operating Cost	$/year	¢/1000 gal
Steam, 45¢/1000 lb	111,375	33.75
Electricity, 8 mils/KWH	26,648	8.08
Chemicals	8,503	2.58
Stores and Maintenance Mat'ls.	8,022	2.43
Maintenance Labor	19,780	6.00
Operating Labor	40,659	12.32
Total	214,987	65.16
Indirect Operating Cost		
Payroll Extras	9,670	2.93
General and Administrative Overhead	17,527	5.31
Taxes and Insurance	31,648	9.59
Amortization	118,727	35.98
Interest on Working Capital	2,858	0.87
Total Cost	395,417	119.84 or $1.20

B. Revised Plant Economics

The capital equipment for the two revised plant operations are the same, with only small differences in size. Equipment varies from that in the present plant by the replacement of exchangers 201, 208, 209, 210, and 211 with flash tanks, and by the addition of an ion-exchange unit for sea-water feed pretreatment.

1. Revised 275°F Plant

The capital cost of the revised plant changed by the removal of the heat exchangers, at $30,820, and the addition of an ion-exchange unit $53,415. The recommendations included in this report were incorporated in the estimation of the capital cost, Table VI-B-1-I.

Erection and assembly, engineering and start-up for the revised plant are the same as for the present plant. The total capital cost is $1.13 per gallon of daily capacity.

The chemical consumption is 1488 pounds per day of H_2SO_4, 396 pounds per day of NaOH, and 105 pounds per day of $Ca(OH)_2$. The resin make-up would be 22 cubic feet per year.

Operating costs were estimated from revised heat and material balances, Section III-B-2. Steam, chemicals, and resin consumption were calculated from the balance. Electric power consumption was taken from the recommended pump changes for the revised plant. Labor costs are the same as those used for the present plant. The cost of water, Table VI-B-1-II, of $0.95 per thousand gallons was calculated from the annual operating cost and the production estimated from the revised 275°F heat and material balance.

TABLE VI-B-1-I

CAPITAL COST FOR REVISED 275°F PLANT

Principal Items of Equipment		
1.	Evaporator Effects	$ 608,396
2.	300-Series Exchangers	104,377
3.	200-Series Exchangers	51,058
4.	312 Condenser	24,215
5.	Deaerator	19,822
6.	Flash Tanks	12,652
7.	Pumps	87,587
8.	Vacuum and Air Compressors	14,878
9.	Acid and Caustic Systems	5,630
10.	Sea-Water Intake	49,317
11.	Desuperheater	2,080
12.	Electrical and Piping	137,014
13.	Product Storage Tank	3,500
14.	Ion-Exchange Unit	53,415
TOTAL PRINCIPAL ITEMS OF EQUIPMENT		$1,173,941
15.	Erection and Assembly	163,342
16.	Instruments	52,202
17.	Operations Buildings	42,800
18.	Land	3,000
19.	Engineering	167,000
20.	Start-Up	22,000
TOTAL CAPITAL COST		$1,624,285
CAPITAL COST PER GALLON OF DAILY CAPACITY		$1.13

TABLE VI-B-1-II

ESTIMATED COST OF WATER
REVISED 275°F PLANT OPERATION

Plant Data

Plant Capacity, million gpd		1.433
Annual Production, millions of gallons		472.870
Economy Ratio, gross lb water/lb steam		11.1
Capital Cost, dollars		1,624,285
Direct Operating Cost	$/year	¢/1000 gal
Steam, 45¢/1000 lb	159,910	33.82
Electricity, 8 mils/kwh	25,041	5.30
Chemicals	9,726	2.06
Resin	517	0.14
Stores and Maintenance Mat'ls.	8,122	1.72
Maintenance Labor	20,029	4.24
Operating Labor	40,659	8.60
Total	264,004	55.88
Indirect Operating Cost		
Payroll Extras	12,833	2.71
General and Administrative Overhead	18,380	3.89
Taxes and Insurance	32,046	6.78
Amortization	120,199	25.42
Interest on Working Capital	3,254	0.69
Total Cost	450,716	95.37 or $0.95

B. Revised Plant Economics

2. Revised 300°F Plant

The revised capital cost, Table VI-B-2-I, includes the required changes to the heat exchangers, the addition of the $86,548 ion-exchange unit and the replacement of the Effect-XII heat exchanger. Engineering, erection and assembly, and start-up are the same as for the present plant. The capital cost is $0.93 per gallon of daily production.

The chemical consumption is 1753 pounds per day of H_2SO_4, 466 pounds per day of NaOH, and 131 pounds per day of $Ca(OH)_2$. The resin make-up would be 73 cubic feet per year.

The cost of water, Table VI-B-2-II, of $0.83 per thousand gallons was calculated for the 300°F revised plant operation. Steam, chemicals, and resin consumption were calculated from the revised 300°F heat and material balance. Power consumption was calculated from the recommended pump changes. Labor costs were the same as the costs used for the present plant. Water cost was calculated from annual operating cost and revised annual production for 300°F operation.

TABLE VI-B-2-I

CAPITAL COST FOR REVISED 300°F PLANT

Principal Items of Equipment	
1. Evaporator Effects	$ 619,567
2. 300-Series Exchangers	117,020
3. 200-Series Exchangers	49,712
4. 312 Condenser	29,267
5. Deaerator	19,822
6. Flash Tanks	12,652
7. Pumps	80,886
8. Vacuum and Air Compressors	14,898
9. Acid and Caustic Systems	5,630
10. Sea-Water Intake	49,317
11. Desuperheater	2,450
12. Electrical and Piping	137,014
13. Product Storage Tank	3,500
14. Ion-Exchange Unit	86,548
TOTAL PRINCIPAL ITEMS OF EQUIPMENT	$1,228,283
15. Erection and Assembly	163,342
16. Instruments	52,202
17. Operations Buildings	42,800
18. Land	3,000
19. Engineering	167,000
20. Start-Up	22,000
TOTAL CAPITAL COST	$1,678,627
CAPITAL COST PER GALLON OF DAILY CAPACITY	$0.93

TABLE VI-B-2-II

ESTIMATED COST OF WATER
REVISED 300°F PLANT OPERATION

Plant Data

Plant Capacity, million gpd		1.812
Annual Production, millions of gallons		598.035
Economy Ratio, gross lb water/lb steam		11.1
Capital Cost, dollars		1,678,627

Direct Operating Cost	$/year	¢/1000 gal
Steam, 45¢/1000 lb	200,821	33.58
Electricity, 8 mils/kwh	25,513	4.27
Chemicals	11,482	1.92
Resin	1,715	0.28
Stores and Maintenance Mat'ls.	8,393	1.40
Maintenance Labor	20,707	3.46
Operating Labor	40,659	6.90
Total	309,290	51.81
Indirect Operating Cost		
Payroll Extras	9,819	1.64
General and Administrative Overhead	17,796	2.98
Taxes and Insurance	33,072	5.53
Amortization	124,216	20.77
Interest on Working Capital	3,594	0.60
Total Cost	497,787	83.33 or $0.83

C. Normalized Plant

The capital cost, Table VI-C-I, was estimated from the criteria set by Bechtel Corporation(5). The major equipment changes were the addition of an ion-exchange unit at $67,400, and the redesign of the 200-series exchangers. Only two 200-series exchangers were needed to fill the requirements of the heat and material balance, Figure III-C-1. The costs of insulation and painting were combined because of the use of insulation that does not require painting. The capital cost is $1.52 per gallon of daily capacity which is $0.08 per gallon of daily capacity less than the present plant capital.

Electrical costs were based on a load requirement of 556 horsepower, and the procedure presented by Bechtel(5). Chemicals used included 1062 pounds per day of sulfuric acid and 282 pounds per day of sodium hydroxide. The resin make-up would be 45 cubic feet per year.

Labor costs were based on one operator per shift, one extra day operator, and a supervisor charging half time to the plant.

Operating cost estimation followed the Bechtel procedure. Fuel requirements were based on steam requirements for the normalized balance. The cost of water, Table VI-C-II, is $1.16 per thousand gallons. This is a reduction of $0.04 from water costs of the present plant. The water cost of $1.16 per thousand gallons for the normalized plant compares very favorably with costs previously presented(6). Bechtel reports the water cost for the normalized long-tube, vertical, distillation plant at $1.46 per thousand gallons and the normalized multi-stage flash plant at $1.30 per thousand gallons(6)(7).

TABLE VI-C-I

CAPITAL COST FOR NORMALIZED PLANT
ONE MILLION GALLONS PER DAY

Principal Items of Equipment		
1.	Evaporator Effects	$ 499,000
2.	Deaerator Equipment	16,500
3.	Heat Exchangers	123,900
4.	Pumps and Drivers	86,100
5.	Desuperheater	4,650
6.	Flash Tanks	15,600
7.	Air Compressor and Vacuum Equipment	11,460
8.	Acid and Caustic Equipment	5,860
9.	Sea-Water Screen	26,000
10.	Ion-Exchange Unit	67,400
11.	Sea-Water Intake Piping	14,000
12.	Electrical	80,000
13.	Boiler	150,000
TOTAL PRINCIPAL ITEMS OF EQUIPMENT		$1,100,470
Erection and Assembly of Plant		
14.	Site Development	38,270
15.	Concrete	17,600
16.	Overhead Crane	9,730
17.	Insulation)	57,300
18.	Painting)	
19.	Spare Parts	21,200
20.	Miscellaneous	34,500
TOTAL ERECTION AND ASSEMBLY OF PLANT		$ 178,600
Other		
21.	Instruments	35,000
22.	Operating Building	44,500
23.	Land	20,000
24.	Engineering	110,000
25.	Start-Up	30,000
TOTAL OTHER		$ 239,500
TOTAL CAPITAL COST		$1,518,570
CAPITAL COST PER GALLON OF DAILY CAPACITY		$1.52

TABLE VI-C-II

ESTIMATED COST OF WATER NORMALIZED PLANT

Plant Data

Plant Capacity, million gpd	1
Annual Production, millions of gallons	330
Economy Ratio, net lb water/lb steam	9.3
Capital Cost, dollars	1,518,570

Direct Operating Cost	$/year	¢/1000 gal
Fuel	122,820	37.22
Electricity	22,656	6.78
Chemicals	6,711	2.03
Resin	1,058	0.32
Stores and Maintenance Mat'ls.	7,443	2.26
Maintenance Labor	18,607	5.64
Operating Labor	37,624	11.40
Total	216,919	65.65
Indirect Operating Cost		
Payroll Extras	8,997	2.73
General and Administrative Overhead	16,307	4.94
Taxes and Insurance	29,771	9.02
Amortization	112,374	34.05
Interest on Working Capital	2,795	0.85
Total Cost	387,163	117.24 or $1.17

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APPENDIX A

THE EFFECT OF TUBE GEOMETRY AND MAL DISTRIBUTION ON HEAT TRANSFER IN LTV EVAPORATORS OF THE FREEPORT DEMONSTRATION PLANT TYPE

For

Dow Chemical Company
Purchase Order B-38286

15 July 1964

Copy No.____
(21,700)

A. E. Dukler
Vice-President, Technical Director

THE EFFECT OF TUBE GEOMETRY AND MAL DISTRIBUTION ON HEAT TRANSFER IN LTV EVAPORATORS OF THE FREEPORT DEMONSTRATION PLANT TYPE

15 July 1964

INTRODUCTION

The Dow Chemical Company has undertaken an engineering evaluation of the Freeport Demonstration Plant under contract to the Office of Saline Water. As part of this evaluation and under sub-contract to Dow, the Houston Research Institute (HRI) has studied the effect of tube geometry on the heat transfer in the LTV evaporator system. This work follows logically and is an extension of earlier studies on the subject of heat transfer in falling film systems done by HRI for the Office of Saline Water.

Vaporization processes are well established as methods to recover fresh water from saline water sources. There are no questions concerning their operability. The questions which remain are concerned exclusively with the economics of the process for large scale use. Many factors enter into this question of economics. These are, of course, the interrelated problems involving maximum allowable temperatures, thermodynamic efficiencies, equipment type selection, process flows, scaling and scale prevention techniques and the manner in which these factors interact to influence capital and product cost. Once a given set of operating conditions are selected and once methods of scale control and level of temperature are specified the central problem becomes one of selecting the heat transfer surface so as to maximize the heat flux, or minimize the cost of the surface involved. The HRI study has been directed toward developing general methods to answer this last question and to provide specific answers for the conditions of operation of the Freeport Demonstration Plant.

This report presents the method of attack on this problem, discusses the computer programs developed and presents a summary of results. Detailed results of the numerous computer runs appear in a computer output appendix containing approximately 230 pages of output.

OBJECTIVES

The original objective of this study was to determine the number of tubes required in certain of the effects of the Freeport Plant as tube diameter and length was varied. Because of the complexity of this problem and the large number of cases to be calculated it was decided to develop a generalized computer program which incorporated these calculations with complete rigor. Thus, shortly after the start of the project a second objective evolved: develop a generalized computer program which would permit the calculation of the number of tubes required for any LTV type plant once the operational characteristics were specified (feed rate, composition and temperature, vacuum level, heat transfer rate, etc.)

The majority of the work was required to accomplish this last objective with the development of information for specified conditions of the Freeport Plant being evolved rather quickly near the end of the study. The objectives can thus be summarized as follows:

A. General Objectives: Develop a generalized design program for an LTV evaporator system which will predict the transfer area or number of tubes for saline water conversion once (1) operational data and (2) any condition of tube diameter and length are specified. The program is to include internal calculation of local heat transfer coefficients, pressure drop and temperature driving force and include a procedure for integrating changes in these quantities up the tube. To the maximum degree possible the program is to include internal calculation of fluid properties and boiling point rise based on curve fits of existing data. The program is to be structured so that as improved data or correlations become available they can readily be incorporated into the existing program and an improved calculational method evolved.

B. Specific Objectives: In order to provide data directly applicable to the Freeport Plant evaluation it was decided to calculate the number of tubes required for each of the following conditions:

1. Variation of Number of Tubes Required as Tube Size and Length Are Varied: (Operating conditions constant without recirculation)

Effect 1	Tube dia's. = 1" & 2" Tube lengths = 20, 24, 30 ft. (No. of cases = 6)
Effect 8	Tube dia's. = 1, 2, 3, 4" Tube lengths = 8, 12, 16, 20, 24, 30 ft. (No. of cases = 24)
Effect 12	Tube dia's. = 2, 3, 4" Tube lengths = 8, 12, 16, 20 ft. (No. of cases = 8)

All of the above cases to be based on a triangular pitch of 1.25 times tube diameter.

2. Result of Introducing Brine Recirculation On Number of Tubes Required: (Tube geometry constant at 2" diameter and 24 ft. long)

Effects 1 & 12	Recirculation rates of 100%, 200%, 300% of normal feed rate (No. of cases = 6)

Above calculation to be based on triangular pitch of 1.25 times tube diameter.

3. Result of Mal-distribution on Number of Tubes Required and on Local Concentrations in Liquid Deficient Region:

Effects 1 & 12	Local flow rates maldistribute into three zones with local rates as low as 80% of normal.

4. Result of Decreased Spacing Between Tubes With 24 Ft. Long Tubes:

Effects 8 & 12	3 inch tubes on 3-1/2" pitch 4 inch tubes on 4-1/2" pitch

APPROACH

Computer Programming: Fortran IV was selected for programming and the philosophy of the program oriented to the use of the very fast machines such as the IBM 7090 series. It was considered desirable to write subroutines for the calculation of all physical properties, vapor pressure relationships, boiling point rise, etc. as a function of composition and temperature. In this way these quantities could be calculated at each point up the tube and the need for arbitrary estimating procedures eliminated. Standard curve fitting techniques were used in every case.

Calculations for the Freeport Plant Conditions: In calculating the design area on number of tubes it is necessary to fix the amount of heat transferred, the flow rate to the effect and its temperature and concentration. In making these calculations for any effect at Freeport, it was assumed that the heat transfer rate would be unchanged by the change in tube diameter or length. Actually, significant changes in size of tubes for the various effects can be expected to shift the distribution of heat somewhat between effects. However, such change can be expected to be small.

COMPUTER PROGRAM

Introduction: A design computer program has been developed for predicting the total area required (tube number) for the long tube vertical (LTV) evaporator. The background theory that forms the basis of this work was first published in 1960(1). Application of the principles to the LTV Evaporator system were published in a report for OSW in 1963(2). It was found that when the theory was applied to certain pilot plant data for LTV evaporators the predictions were very satisfactory. This work incorporates all of the above experience to develop a design program. Due to the complex and tedious nature of the equations for predicting interfacial shear and two-phase flow pressure drop, it was advantageous to develop this calculation for use on an electronic computer. Use was made of the Fortran IV language(3) and the IBSYS-IBJOB operating system processor(4). Development of this computer program permits the study of the parameters which influence the design of the LTV evaporator to a degree never before accomplished.

Approach: The basic purpose of this program is to take external process conditions and produce a mechanical design (total heat transfer area) which will operationally reproduce these same process conditions. The program was written such that the mechanical parameters of tube length and tube diameter as well as the process factors (such as heat transfer rate, flow rate, properties, temperature, pressure) could be varied external to the program. The total heat transfer area can be minimized by exploring the effect of variables. Whether or not this minimum is the optimum design depends on subsequent analysis of construction cost for the various mechanical designs.

To predict the heat transfer for the LTV evaporator it is necessary to set up a mathematical model to describe the system. The local heat transfer coefficient (h) for vertical falling films can be described mathematically as follows:

h = (NRE, β , physical properties)
NRE = Reynolds Number = 4W/
W = Flow Rate of Liquid
D = Diameter of the tube
μ_L = Viscosity of the liquid
β = Interfacial shear (dimensionless) between liquid and vapor interface

This dimensionless parameter (β) was defined by Dukler(2) as

$$\beta = \frac{(dP/dL)_{TP}\, D\, g_L^{1/3}}{4\, \rho_L^{1/3}\, \mu_L^{2/3}}$$

where

$(dP/dL)_{TP}$ = axial pressure gradient due to frictional energy loss in two-phase flow.

ρ_L = density of liquid

Therefore, it can be seen that it is necessary to predict the two-phase flow pressure drop in order to completely define this system. Using the approach of Martinelli to define the two-phase pressure drop, beta (β) can be shown to be:

$$\beta = A\,(\mathrm{RELI} - \mathrm{RELX})^{1.4}\,\mathrm{RELX}^{0.4}$$

$$\text{where } A = \frac{0.250\,\mu_L^{1.173}\,\mu_G^{0.160}}{g_L^{2/3}\,D^2\,\rho_L^{0.553}\,\rho_G^{0.280}}$$

RELI = Inlet Reynolds number to the tube

RELX = Local Reynolds numbers at a point in the tube.

Beta (β) varies from zero at the inlet of the tube (non-flashing feed) to a maximum at the tube outlet. Therefore, to mathematically describe this model it is necessary to perform a numerical integration, either up or down the tube, to account for the effect of the change in beta (β), the Reynolds number of the liquid and vapor, and physical properties on the local heat transfer coefficient. For purposes of this program the following model was set up to perform this integration.

Block Diagram (Drawing #D-101-21,700 p. 19): The block diagram method was used to set up the basic paths of information flow which is necessary to perform this integration, describe all of the alternates of flashing feed and sensible heating conditions, and print out the results in a suitable manner. The calculational procedure used was as follows: (See Nomenclature p.31ff and Figure 1 to follow this discussion).

1. Based on an initial assumption of an overall coefficient of heat transfer (UC) (input data) estimate an initial value of the tube number (TN).

2. Calculate the process flows, liquid and vapor, into and out of one tube

3. Set up and initiate the numerical integration loop. (See Figure 1) This integration is carried out as follows:

    a. Choose and incremental tube length, DL, (input data).

    b. Set up initial values of the accumulative registers equal to zero. (i.e. TLX, Q, W, and V). The purpose of the above registers are as follows:

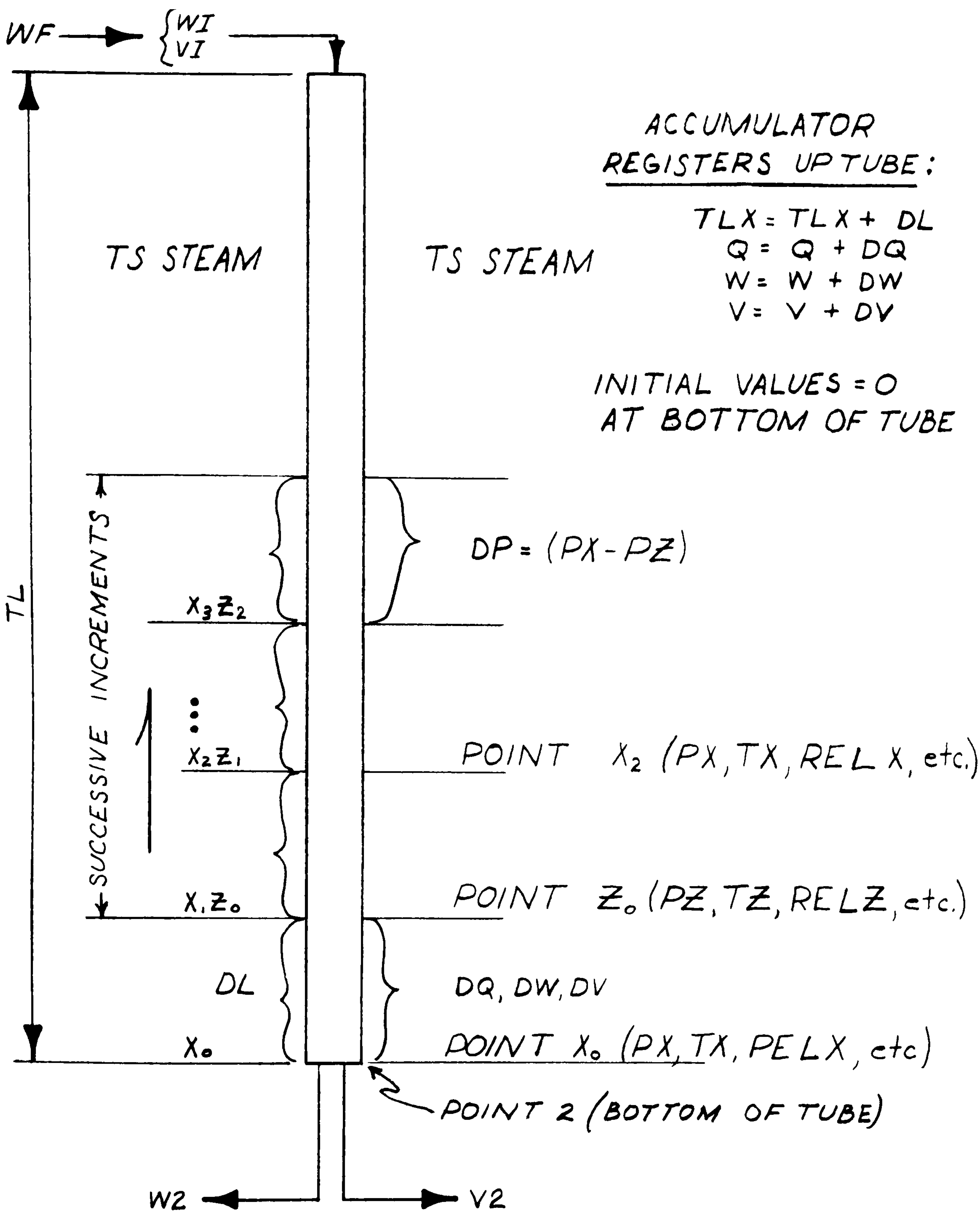


FIGURE 1

MATHEMATICAL MODEL
FOR
LVT EVAPORATOR

TLX: tube length from bottom of tube to point X: This parameter monitors the integration up the tube and determines that one trial is complete when TLX = TL.

Q: accumulative heat that is transferred through the tube wall from the bottom of the tube to point X: This parameter monitors the convergence of the heat balance and determines when the calculated heat transferred equal the design heat transfer (Q x TN = QS).

W: accumulative vaporization rate from the bottom of the tube to point X: This parameter monitors the limits of initial approximations of TN, forms the basis for the point material and energy balances and determines the flow regime Reynolds number.

V: accumulative flash vapor rate: starting at at the bottom of the tube to point X. This parameter accumulates the amount of vapor produced by flashing due to pressure drop rather than heat transfer. This accumulation becomes very important in the vacuum evaporators because it changes the point distribution of liquid and vapor up the tube. (i.e. at any point X up the tube--WLX = WB + W + V) where WB equals the bottom liquid rate.

The differential (or incremental) values of these three registers (i.e. DQ, DW, and DV) then represent the incremental change over the incremental length DL.

c. To initiate the numerical integration it is assumed that the temperature difference between the steam and saline at the bottom of the tube, (Point X) is approximately equal to the difference at point X_c.

This then allows the following sequence of calculations across DL.

DTA:= $\left[(TS-T_{x_o}) + (TS-T_{z})\right] / 2 \equiv (TS-T_{x_o})$

DQ = (UC) (Constant x DL) (DTA); Q = Q + DQ

DW = DQ/Latent Heat, W = W + DW

DV = DQV/Latent Heat; V = V + DV

WLX = WB + W + V

DP = ϕ(RELX, REGX, DL, β , Physical properties)

PX = P + DP

TXS = ϕ(PX, TRI, PRI, CC)

TX = TXS + BPRX

then: DTAX (at point X-calculated) equals

DTAX = (DTZ + TS - TX) / 2

The calculated value of the average temperature difference across the increment for heat transfer is then compared to the initial assumption. If they are not equal to within .005°F, the DTA is set equal to DTAX and the whole procedure is repeated until convergence occurs. This gives us a completely balanced heat and material balance loop upon which the calculation of the theoretical heat transfer coefficient is based.

d. Calculate the theoretical heat transfer coefficient for increment DL. as

HXA = ϕ (RELX, β , Nusselt No., Physical Properties)

and

HSA (steam side) = ϕ (RESX, $\underline{\beta = 0}$, Nusselt No., Physical Properties).

The basic data used to calculate the individual heat transfer coefficients was taken from the OSW Report (2), pages 84 through 87, Figures 6-9. These curves were equation fit for computer use. For the steam side, the interfacial shear, β , was assumed to be zero; therefore the $\beta = 0$ curve was used. The equations were of such a form that they included the Prandtl number variation. They were fit for two regions of interfacial shear:

$$\beta \leqq 100 \; ; \; \beta > 100$$

e. Calculate the overall coefficient of heat transfer (UCA) for increment DL.

UCA is then compared to the original (or former) value of UC to within .01. If convergence is not accomplished, then UC is set equal to UCA and the procedure is repeated for the increment DL until all values of the heat and material balance loop and the theoretical heat transfer coefficient loop are satisfied within specified limits. If they are, then TLX is incremented as TLX = TLX + DL, values at point X are made point Z, and the integration procedure continues up the tube.

4. Sensible Heating Routines: After each increment of convergence around the integration loop, a check is made to determine whether or not there is sufficient pressure drop to induce sensible heating in the tube (i.e. $TX \geqq TF$). If sensible heating has been induced, then the overall heat balance is checked to see if we are in the limits of the total design heat duty. If not, then the design tube number is adjusted and the calculations started again from the beginning.

If sensible heating has not occurred then the integration is continued up the tube (as a flashing feed case), continually checking for sensible heating initiation at each increment.

5. Tube Number Modification: The overall design (tube number) is modified when the following conditions occur:

   a. $W > VB$ - This indicates a basic discrepancy in the heat and material balance loop which is outside the limits of overall convergence.

   b. TLX = TL - This occurs for two different cases as follows:

      Flashing Feed Case: Integration has proceeded to the complete tube length and convergence on the total heat duty has not occurred.

      Sensible Heating Case: Integration is completed as above, but through both regions without convergence of the total heat duty to that specified (i.e. Qs). The tube number from one trial to another is modified on the principle that the change in the number of tubes from one trial to another should be a direct function of the difference between the calculated heat duty and the design heat duty; PLUS OR MINUS: the change in tube number is based on the average heat duty per tube of the previous calculation.

Included in the program is a self-checking routine that eliminates the possibility of calculating the same tube number twice (i.e. initiation of an infinite looping situation).

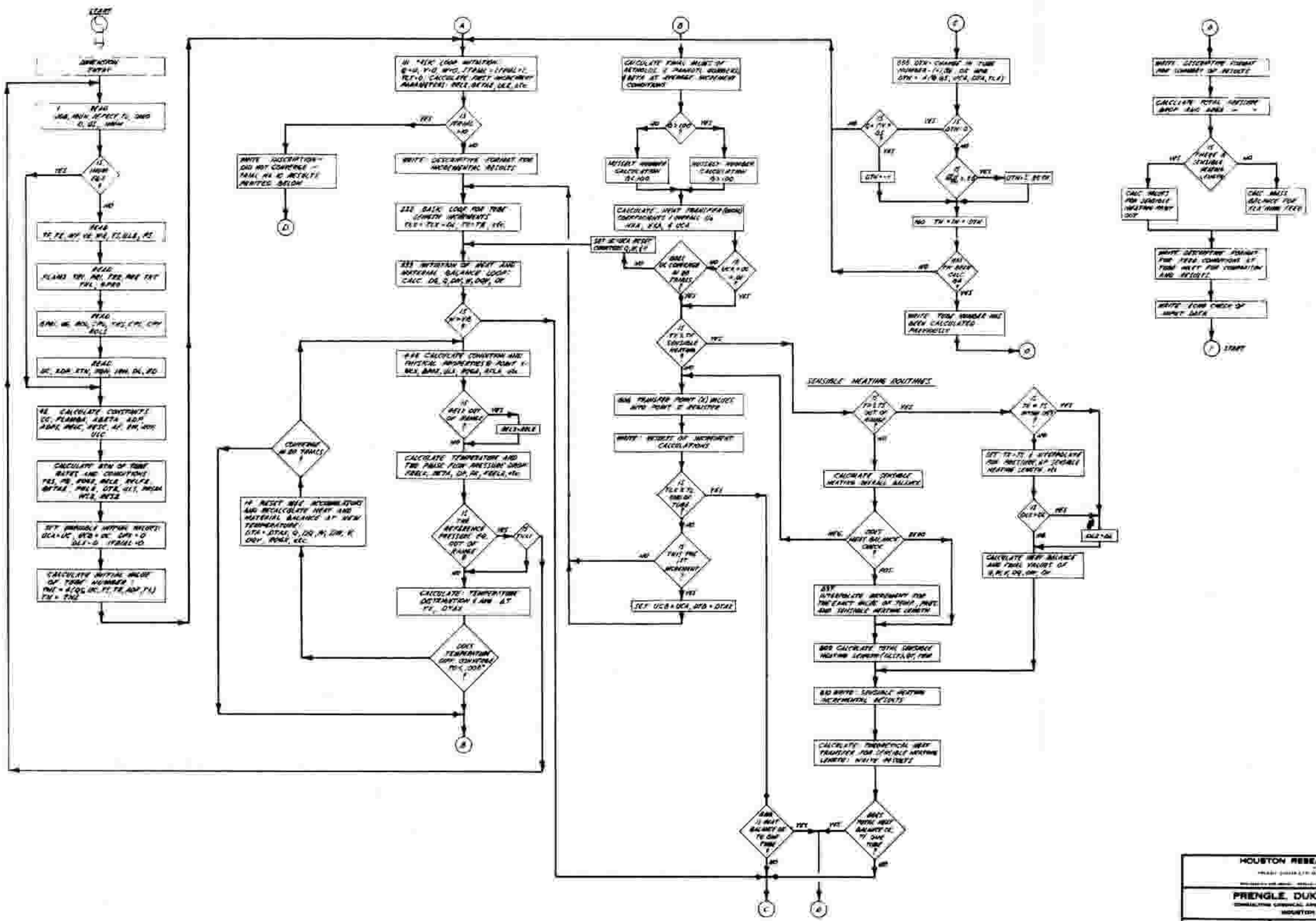
6. Final Convergence: Final convergence is accomplished to within one (1) tube. The results are summarized on one (1) sheet with the input data for convenience in interpretation.

Freeport Plant Application: To check out the theoretically predicted designs, a complete calculation was performed on Effects Nos. I, VIII, and XII using the present mechanical design parameters. The predicted total area of heat transfer was in very good agreement with the actual design. To match the actual design and to evaluate the effect of fouling on the evaporators, the following fouling and pressure drop equation factors were used:

Effect Number	ΔP Eq. Constant	Fouling Factor	Predicted* Tube No.	Actual* Tube No.
I	2.0	.00097	502	490
VIII	2.0	.00015	490	490
XII	2.0	.00125	560	554

* Tubes were all 18 BWG, Al-BR, 2" O.D., 24' long.

Program Printout: A detailed printout of the program in Fortran IV appears immediately following the block diagram. Typical pages of printout are included to show the output format. Program nomenclature is defined in a listing which follows the output sheets.



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HOUSTON, TEXAS

REVISIONS

BLOCK DIAGRAM
HRI PROGRAM FOR LTV EVAPORATOR
HEAT TRANSFER CALCULATIONS

DRAWN BY CSR
DWG. NO. D-731
-81,700

PROJECT 21,700
PROGRAM LISTING

```
      DIMENSION TNTRY(20)
    1 READ(5,2) JOB,IRUN,IEFECT,TL,DIAO,D,QS,INUM

    2 FORMAT(     3I10,3F10.5,F10.0,I10)
      IF(INUM.EQ.1) GO TO 42
      READ(5,3) TF,T2,WF,V2,W2,TS,UL2,PS
    3 FORMAT(     2F10.4,3F10.0,3F10.5)
      READ(5,4) FLAMS,TR1,PR1,TR2,PR2,TKT,TKL,BPRO
    4 FORMAT(     8F10.4)
      READ(5,5) BPRI,UG,ROL,CPL,TKS,CPS,CPV,ROLS
    5 FORMAT(     8F10.5)
      READ(5,6) UC,XDP,XTN,XQN,IRN,DL,RD
    6 FORMAT(     4F10.5,I10,F10.5,F10.8)
   42 TF=TF+460.
      T2=T2+460.
      TR1=TR1+460.
      TR2=TR2+460.
      TS=TS+460.
      US=UC
      CC=TR2*TR1/(TR2-TR1)*ALOG(PR2/PR1)
      FLAMBA=1.987*CC/18.
      ABETA=6.470E-5/D/D*UG**.156/ROL**.553*XDP
      ADP=5.875E-8/D/D/D*UG**.156/ROL**.22
      ADPS=5.393E-9/D/D/D
      RELC=15.2788/D
      RESC=15.2788/DIAO
      AF=D/DIAO
      RW=(DIAO-D)/TKT/(AF+1.)/12.+RD
      AOF=.2618*DIAO
      ULC=(UL2-(5.549-8475./T2+3.504E6/T2/T2))*EXP(.0116*T2)/BPRO
      T2S=T2-BPRO
      P2=PR1*EXP(CC*(T2S-TR1)/T2S/TR1)
      ROG2=.82539*P2/T2+.2508*P2*P2/T2/T2
      TNI=FLOAT(IFIX(QS/(UC*(TS-T2))/AOF/TL+.5))
      REL2=RELC*W2/UL2/TNI
      RELF2=RELC*WF/UL2/TNI
      BETA2=ABETA*UL2**1.177/ROG2**.78*(RELF2-REL2)**1.404*REL2**.39
      PRL2=CPL*UL2/TKL
      DT2=TS-T2
      TN=TNI
      ULS=5.549-8475./TS+3.504E6/TS/TS
      PRSXA=CPS*ULS/TKS
      WS2=QS/FLAMS
      RES2=RESC*WS2/ULS/TN
      UCA=UC
      UCB=UC
      DPX=0.
      DLX=0.
      ITRIAL=0
  111 Q=0.
      V=0.
      ITRIAL=ITRIAL+1
      IF(ITRIAL.GT.10) GO TO 998
      J=ITRIAL
      IF(DL.LT.2.0) GO TO 218
```

```
      IF(J-2) 217,219,220
  220 IF(J-4) 218,219,221
  221 IF(J-6) 218,219,223
  223 IF(J-8) 218,219,224
  224 IF(J-10) 218,219,217
  218 WRITE(6,7)
      GO TO 217
  219 WRITE(6,70)
  217 WRITE(6,8)
    8 FORMAT(27X,57HHRI PROGRAM FOR LTV EVAPORATOR HEAT TRANSFER CALCULA
     1TIONS)
      WRITE(6,9)
    9 FORMAT(1H0,19X,74HPROJECT   21,700   -   DOW CHEMICAL COMPANY   -   OS
     1W FREEPORT PLANT EXPANSION/1H )
      WRITE(6,10) IRUN,TL,DIAO,IEFECT
   10 FORMAT(10X,10HRUN NUMBER,I6,5X,13HTUBE LENGTH= ,F4.1,4H FT.,5X,14H
     1TUBE DIAMETER=,F6.3,12H INCHES O.D.,5X,10HEFFECT NO.,I3/1H )
      WRITE(6,11) ITRIAL,TN,XDP
   11 FORMAT(10X,12HTRIAL NUMBER,I5,4X,11HTUBE NUMBER,F7.0,12X,37HPRESSU
     1RE DROP EQUATION MULTIPLIED BY ,F4.2/1H0)
      WRITE(6,12)
   12 FORMAT(10X,6HLENGTH,6X,9HHEAT DUTY,6X,9HPRESSURE,6X,11HTEMPERATURE
     1,6X,7HDELTA T,6X,12HREYNOLDS NO.,6X,9HOVERALL U)
      WRITE(6,13)
   13 FORMAT(12X,3HFT.,9X,6HBTU/HR,8X,6HIN. HG,10X,7HDEG. F.,9X,7HDEG. F
     1.,22X,12HBTU/HR FT2 F/1H )
      TNTRY(J)=TN
      W=0.
      TLX=0.
      DTA=DT2
      DTZ=DT2
      WB=W2/TN
      VB=V2/TN
      VZ=VB
      TZ=T2
      PZ=P2
      WSZ=WS2/TN
      RELZ=RELC*WB/UL2
      RELFZ=RELC*WF/UL2/TN
      FRELZ=(RELFZ-RELZ)**1.404*RELZ**.396
      BETAZ=ABETA*UL2**1.177/ROG2**.78*FRELZ
      PRLZ=PRL2
      ULZ=UL2
      WZ=WB
      RESZ=RESC*QS/FLAMS/TN/ULS
      ROGZ=ROG2
  222 TLX=TLX+DL
      TX=TZ
      ROGX=ROGZ
      IUCA=0
  333 DQ=AOF*UC*DTA*DL
      Q=Q+DQ
      DW=DQ/FLAMBA
      W=W+DW
      DQV=(WZ+DW/2.)*CPL*(TX-TZ)
      DV=DQV/FLAMBA
```

```
      V=V+DV
      IDTA=0
      IF(VB-W) 555,555,444
  444 WLX=WB+W+V
      BPRX=BPRO-(W+V)*TN*(BPRO-BPRI)/V2
      ULX=5.549-8475./TX+3.504E6/TX/TX+ULC*BPRX/EXP(.0116*TX)
      ULA=(ULX+ULZ)/2.
      ROGA=(ROGX+ROGZ)/2.
      RELX=RELC*WLX/ULX
      RELFX=RELC*WF/ULX/TN
      IF(RELX.LT.RELFX) GO TO 440
      RELX=RELZ
  440 FRELX=(RELFX-RELX)**1.404*RELX**.396
      BETA=ABETA*FRELX*ULX**1.177/ROGX**.78
      FRELA=(FRELX+FRELZ)/2.
      DP=ADP*FRELA*ULA**1.844/ROGA**.78*XDP*DL
      PX=PZ+DP
      IF(PX.GE.PR2) GO TO 130
      TXS=TR2/(1.+TR2/CC*ALOG(PR2/PX))
      TX=TXS+BPRX
      DTAX=(DTZ+TS-TX)/2.
      IF(ABS(DTAX-DTA).LT..005) GO TO 15
   14 DTA=DTAX
      WLX=WB
      Q=Q-DQ
      DQ=AOF*UC*DTA*DL
      Q=Q+DQ
      W=W-DW
      DW=DQ/FLAMBA
      W=W+DW
      V=V-DV
      DQV=(WB+W+V-DW/2.+DV/2.)*CPL*(TX-TZ)+(VB-V-DV/2.-W+DW/2.)*CPV*(TX-
     1TZ)
      DV=DQV/FLAMBA
      V=V+DV
      ROGX=.82539*PX/TX+.2508*PX*PX/TX/TX
      IDTA=IDTA+1
      IF(IDTA.GE.20) GO TO 15
      GO TO 444
   15 RELXA=(RELX+RELZ)/2.
   16 IF(TN*Q.GE.QS) GO TO 140
      WSX=WS2/TN-Q/FLAMS
  140 RESX=RESC*WSX/ULS
      RESXA=(RESX+RESZ)/2.
      PRLX=CPL*ULX/TKL
      PRLXA=(PRLX+PRLZ)/2.
      BETAA=(BETA+BETAZ)/2.
      IF(BETAA.GE.100.) GO TO 777
      H1=.1674*PRLXA**.44+.023285*BETAA**.671*PRLXA**.2695
      H2=.1950*PRLXA**.44+.024692*BETAA**.620*PRLXA**.306
      GO TO 17
  777 H1=.1674*PRLXA**.44+.09375*BETAA**.3925*PRLXA**.329
      H2=.1950*PRLXA**.44+.05008*BETAA**.475*PRLXA**.385
   17 AH=ALOG(H2/H1)/1.0975
      HXN=H1*(RELXA/2000.)**AH
      HXA=746.*HXN*ROL**.667*TKL/ULX**.667
```

```
      HSN=1.1/RESXA**.333+.000912*RESXA**.617*PRSXA**.668
      HSA=746.*HSN*ROLS**.667*TKS/ULS**.667
      UCA=1./(1./HSA+1./(HXA*AF) +RW)
      IF((UCA-UC)*(UCA-UC) -.01)19,19,18
   18 UC=UCA
      IUCA=IUCA+1
      IF(IUCA.GE.20) GO TO 19
      Q=Q-DQ
      W=W-DW
      V=V-DV
      GO TO 333
  808 TZ=TX
      BETAZ=BETA
      ULZ=ULX
      PRLZ=PRLX
      RELZ=RELX
      WZ=WLX
      FRELZ= FRELX
      RESZ=RESX
      DTZ=TS-TZ
      PZ=PX
      TEMP=TZ-460.
      QT=Q*TN
      WRITE(6,20) TLX,QT,PZ,TEMP,DTAX,RELXA,UCA
   20 FORMAT(10X,F5.2,7X,F9.0,6X,F9.5,8X,F6.2,9X,F7.3,9X,F7.0,9X,F6.2)
      TNS=TN
      IF(TLX.GE.TL) GO TO 888
      IF(TLX-DL-.0001)21,21,22
   21 UCB=UCA
      DTB=DTAX
   22 GO TO 222
  888 IF((Q*TN-QS)*(Q*TN-QS).LE.((QS*QS/TN/TN)*XQN)) GO TO 999
  555 DTN=FLOAT(IFIX((QS-Q*TN)*XTN/((UCB+UCA)/2.*(TS-(T2+TZ)/2.)*ADF*TLX
     1)+.5))
      IF(DTN.EQ.0.0) GO TO 150
      TNS=TN
      IF(ABS(DTN/TN).LT..25) GO TO 160
      DTN=FLOAT(IFIX(DTN/ABS(DTN)*.25*TN))
  160 TN=TN+DTN
      DO 180 IDTN=1,J,1
  180 IF(TNTRY(IDTN).EQ.TN) GO TO 190
      GO TO 111
  998 WRITE(6,7)
      WRITE(6,997)
  997 FORMAT(10X,38H DID NOT CONVERGE'TRIAL NO. 10 RESULTS)
      GO TO 996
  999 WRITE(6,7)
  996 WRITE(6,70)
      WRITE(6,70)
      WRITE(6,8)
      WRITE(6,9)
      WRITE(6,10) IRUN,TL,DIAO,IEFECT
      DPT=PZ-P2
      AT=ADF*TL*TNS
      WRITE(6,24)
   24 FORMAT(1H0, 9X,9HHEAT DUTY,9X,9HOVERALL U,9X,10HTOTAL AREA,9X,4HTU
```

```
     1BE,9X,13HPRESSURE DROP,8X,8HDELTA T.)
      WRITE(6,25)
   25 FORMAT(12X,6HBTU/HR,9X,12HBTU/HR FT2 F,10X,7HSQ. FT.,9X,6HNUMBER,1
     12X,6HIN. HG,12X,6HDEG. F)
      WRITE(6,70)
      WRITE(6,26) QT,UCB,AT,TNS,DPT,DTB
   26 FORMAT(10X,F9.0,8X,F6.1,5H 'BTM,8X,F10.2,8X,F6.1,8X,F13.9,8X,F5.2,
     15H -BTM)
      WRITE(6,27) UCA,DTAX
   27 FORMAT(27X,F6.1,5H -TOP,61X,F5.2,5H -TOP)
      WRITE(6,70)
   70 FORMAT(1H0)
      IF(TX-TF+.005) 813,806,806
  813 VI=V2-W*TNS-V*TNS
      TF=TF-460.
      WI=WF-VI
      GO TO 812
  806 VI=0.
      WI=WF
      TF=TF-460.
      TEMP=TF
      WRITE(6,802) DLST
  812 WRITE(6,70)
      WRITE(6,70)
      WRITE(6,28)
   28 FORMAT(32X,55HCALCULATED FEED CONDITIONS AT TUBE INLET FOR COMPARI
     1SON/1H0)
      WRITE(6,29)
   29 FORMAT(1H0,9X,9HFEED RATE,5X,10HFEED TEMP.,5X,11HFEED LIQUID,5X,11
     1HFEED VAPOR ,5X,11HSTEAM CHEST,6X,10HTUBE INLET,5X,10HTUBE INLET)
      WRITE(6,30)
   30 FORMAT(12X,6HLBS/HR,8X,6HDEG. F,10X,6HLBS/HR,9X,6HLBS/HR,7X,12HPRE
     1S. IN. HG,5X,12HPRES. IN. HG,3X,12HTEMP. DEG. F)
      WRITE(6,70)
      WRITE(6,31) WF,TF,WI,VI,PS,PZ,TEMP
   31 FORMAT(8X,F9.0,5X,F10.4,5X,F10.0,6X,F10.1,5X,F10.5,7X,F10.5,7X,F10
     1.5)
      T2=T2-460.
      TS=TS-460.
      TR1=TR1-460.
      TR2=TR2-460.
      WRITE(6,70)
      WRITE(6,70)
      WRITE(6,70)
      WRITE(6,824)
  824 FORMAT(50X,19H PROGRAM INPUT DATA)
      WRITE(6,70)
      WRITE(6,2) JOB,IRUN,IEFECT,TL,DIAO,D,QS,INUM
      WRITE(6,3) TF,T2,WF,V2,W2,TS,UL2,PS
      WRITE(6,4) FLAMS,TR1,PR1,TR2,PR2,TKT,TKL,BPRO
      WRITE(6,5) BPRI,UG,ROL,CPL,TKS,CPS,CPV,ROLS
      WRITE(6,6) US,XDP,XTN,XQN,IRN,DL,RD
      WRITE(6,7)
    7 FORMAT(1H1)
      GO TO 1
  130 IF (TN.LT. 1.01) GO TO 1
```

```
      TNS=TN
      TN=FLOAT(IFIX(1.25*TN+.5))
      WRITE(6,900)TN
  900 FORMAT(11H AT 130,TN=,E15.7)
      DO 200 IDTN=1,J,1
  200 IF(TNTRY(IDTN).EQ.TN) GO TO 190
      GO TO 111
  150 IF(QS-Q*TN) 170,999,999
  170 DTN=-1.0
      GO TO 160
  801 IF(TX-TS-.05) 803,803,804
  804 TX=TS
      TXS=TX-BPRX
      PX=PR1*EXP(CC*(TXS-TR1)/TXS/TR1)
      DPX=PX-PZ
      DLX=DPX/ADP/FRELA/ULA**1.844*ROGA**.78
      TLX=TLX-DL
      IF(DLX.GT.DL) GO TO 803
  805 DLST=TL-TLX+DLX
      TLX=TL-DLST
      TEM=TX-460.
      DTAX=(DTZ+TS-TX)/2.
      Q=Q-DQ
      DQ=AOF*UC*DTAX*DLX
      Q=Q+DQ
      W=W-DW
      DW=DQ/FLAMBA
      W=W+DW
      V=V-DV
      DQV=(WB+W+V-DW/2.+DV/2.)*CPL*(TX-TZ)+(VB-V-DV/2.-W+DW/2.)*CPV*(TX-
     1TZ)
      DV=DQV/FLAMBA
      V=V+DV
      QT=Q*TN
  810 WRITE(6,20) TLX,QT,PX,TEM,DTAX,RELXA,UCA
      TA=(TX+TF)/2.
      DTAS=TS-TA
      ULAS=5.549-8475./TA+3.504E6/TA/TA+ULC*BPRI/EXP(.0116*TA)
      RELAS=RELC*WF/TN/ULAS
      WSX=WS2/TN-Q/FLAMS
      RESXA=RESC*WSX/ULS
      RESXA=RESXA/2.
      PRLAS=CPL*ULAS/TKL
      H1=.1674*PRLAS**.44
      H2=1.1649*H1
      AH=ALOG(H2/H1)/1.0975
      HSNS=H1*(RELAS/2000.)**AH
      HSAS=746.*HSNS*ROL**.667*TKL/ULAS**.667
      HSN=1.1/RESXA**.333+.000912*RESXA**.617*PRSXA**.668
      HSA=746.*HSN*ROLS**.667*TKS/ULS**.667
      UCS=1./(1./HSA+1./(HSAS*AF)+RW)
      DQAS=UCS*AOF*DLST*DTAS
      Q=Q+DQAS
      DPL=ADPS*RELAS**1.80*ULAS**2.0/ROL*DLST
      PZ=PX+DPL
      UCA=UCS
```

```
      TLX=TL
      TEM2=TF-460.
      QT=Q*TN
      WRITE(6,20) TLX,QT,PZ,TEM2,DTAS,RELAS,UCS
      WRITE(6,70)
      WRITE(6,802) DLST
  802 FORMAT(10X,26H SENSIBLE HEATING LENGTH= ,F5.2)
      IF(ABS(Q*TN-QS).GE.QS/TN) GO TO 555
      GO TO 999
  803 DLX=DL
      GO TO 805
  190 WRITE(6,191) TN
  191 FORMAT(1H0,10X,48H TUBE NUMBER HAS BEEN CALCULATED PREVIOUSLY, TN=
     1,F6.2)
      GO TO 999
   19 IF(TX.LE.TF) GO TO 808
      IF(TX.GE.TS) GO TO 801
      DQSEN=WF/TN*CPL*(TX-TF)
      QSEN=Q+DQSEN
      IF(QSEN*TN-QS) 808,809,897
  897 TLX=TLX-DL
      Q=Q-DQ
      W=W-DW
      V=V-DV
      TXIS=(TZ+TX)/2.
      DQSEM=WF/TN*CPL*(TXIS-TF)
      DQI=QS/TN-DQSEM-Q
      DTAX=(DTZ+TS-TXIS)/2.
      DLI=DQI/AOF/UCA/DTAX
      DWI=DQI/FLAMBA
      Q=Q+DQI
      W=W+DWI
      DVI=TXIS/TX*DV
      V=V+DVI
      WLX=WB+W+V
      BPRX=BPRO-(W+V)*TN*(BPRO-BPRI)/V2
      TXI=TXIS-BPRX
      PXI=PR1*EXP(CC*(TXI-TR1)/TXI/TR1)
      RELXA=RELC*(WLX+WZ)/2./ULA
      PX=PXI
      TX=TXIS
      TLX=TLX+DLI
  809 TEM=TX-460.
      DLST=TL-TLX
      QT=Q*TN
      GO TO 810
      END
```

SAMPLE OUTPUT

```
           PROJECT   21,700  -  DOW CHEMICAL COMPANY  -  OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200     TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.     EFFECT NO. 12

TRIAL NUMBER    1    TUBE NUMBER   308.          PRESSURE DROP EQUATION MULTIPLIED BY 2.00

LENGTH       HEAT DUTY       PRESSURE,      TEMPERATURE      DELTA T      REYNOLDS NO.      OVERALL U
 FT.          BTU/HR          IN. HG         DEG. F.         DEG. F.                       BTU/HR FT2 F

 2.00        1123262.        3.78060         125.86          10.568          2669.           329.54
 4.00        2155281.        3.86372         126.64           9.749          2713.           328.21
 6.00        3105784.        3.94012         127.34           9.012          2753.           327.01
 8.00        3983122.        4.01052         127.97           8.345          2791.           325.94
10.00        4794481.        4.07555         128.55           7.740          2826.           324.99
12.00        5546083.        4.13574         129.07           7.189          2858.           324.14
14.00        6243351.        4.19159         129.56           6.685          2888.           323.39
16.00        6891034.        4.24350         130.00           6.222          2916.           322.72
18.00        7493308.        4.29186         130.41           5.797          2942.           322.12
20.00        8053866.        4.33699         130.78           5.404          2966.           321.60
22.00        8575979.        4.37918         131.13           5.041          2988.           321.14
24.00        9062563.        4.41870         131.46           4.703          3010.           320.74

                    HRI PROGRAM FOR LTV EVAPORATOR HEAT TRANSFER CALCULATIONS

           PROJECT   21,700  -  DOW CHEMICAL COMPANY  -  OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200     TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.     EFFECT NO. 12

TRIAL NUMBER    2    TUBE NUMBER   385.          PRESSURE DROP EQUATION MULTIPLIED BY 2.00

LENGTH       HEAT DUTY       PRESSURE,      TEMPERATURE      DELTA T      REYNOLDS NO.      OVERALL U
 FT.          BTU/HR          IN. HG         DEG. F.         DEG. F.                       BTU/HR FT2 F

 2.00        1389656.        3.75035         125.56          10.718          2134.           321.67
 4.00        2705831.        3.80502         126.06          10.186          2168.           320.58
 6.00        3957028.        3.85440         126.51           9.714          2199.           319.62
 8.00        5150881.        3.89893         126.90           9.293          2229.           318.79
10.00        6294205.        3.93901         127.26           8.920          2257.           318.08
12.00        7393127.        3.97496         127.57           8.590          2284.           317.50
14.00        8453198.        4.00709         127.84           8.298          2309.           317.04
16.00        9479489.        4.03568         128.08           8.042          2333.           316.72
18.00       10476664.        4.06097         128.29           7.818          2356.           316.54
20.00       11449111.        4.08318         128.47           7.624          2378.           316.53
22.00       12400804.        4.10250         128.62           7.457          2399.           316.69
24.00       13335671.        4.11912         128.75           7.316          2419.           317.07
```

SAMPLE OUTPUT (Continued -1)

```
              PROJECT    21,700   -   DOW CHEMICAL COMPANY   -   OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200       TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.     EFFECT NO. 12

TRIAL NUMBER     3     TUBE NUMBER    481.           PRESSURE DROP EQUATION MULTIPLIED BY 2.00

LENGTH       HEAT DUTY       PRESSURE,      TEMPERATURE       DELTA T      REYNOLDS NO.       OVERALL U
 FT.          BTU/HR          IN. HG          DEG. F.         DEG. F.                        BTU/HR FT2 F

 2.00         1716945.         3.73010         125.36          10.821           1708.           315.03
 4.00         3376953.         3.76572         125.67          10.487           1737.           314.28
 6.00         4988145.         3.79710         125.94          10.198           1764.           313.70
 8.00         6558091.         3.82450         126.16           9.950           1789.           313.29
10.00         8093872.         3.84821         126.36           9.740           1814.           313.09
12.00         9602007.         3.86845         126.51           9.565           1839.           313.14
14.00        11089420.         3.88544         126.64           9.422           1862.           313.48
16.00        12562406.         3.89940         126.74           9.309           1885.           314.20
18.00        14027687.         3.91054         126.81           9.223           1907.           315.44
20.00        15492645.         3.91906         126.86           9.164           1929.           317.41
22.00        16966135.         3.92516         126.88           9.129           1950.           320.50
24.00        18460392.         3.92909         126.89           9.115           1972.           325.52

                MRI PROGRAM FOR LTV EVAPORATOR HEAT TRANSFER CALCULATIONS

              PROJECT    21,700   -   DOW CHEMICAL COMPANY   -   OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200       TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.     EFFECT NO. 12

TRIAL NUMBER     4     TUBE NUMBER    552.           PRESSURE DROP EQUATION MULTIPLIED BY 2.00

LENGTH       HEAT DUTY       PRESSURE,      TEMPERATURE       DELTA T      REYNOLDS NO.       OVERALL U
 FT.          BTU/HR          IN. HG          DEG. F.         DEG. F.                        BTU/HR FT2 F

 2.00         1957102.         3.72108         125.26          10.868           1489.           311.50
 4.00         3867318.         3.74826         125.49          10.625           1515.           311.03
 6.00         5739140.         3.77171         125.67          10.420           1541.           310.77
 8.00         7580625.         3.79165         125.82          10.252           1565.           310.76
10.00         9399531.         3.80830         125.94          10.116           1589.           311.07
12.00        11203827.         3.82187         126.03          10.012           1613.           311.80
14.00        13001889.         3.83258         126.10           9.936           1636.           313.09
16.00        14803197.         3.84062         126.13           9.887           1658.           315.22
18.00        16619671.         3.84622         126.14           9.863           1681.           318.66
20.00        18469733.         3.84969         126.13           9.861           1704.           324.60
22.00        20390685.         3.85124         126.11           9.880           1727.           336.40
```

SAMPLE OUTPUT (Continued -2)

```
          PROJECT    21,700  -  DOW CHEMICAL COMPANY  -  OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200      TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.      EFFECT NO. 12

TRIAL NUMBER    5     TUBE NUMBER   530.            PRESSURE DROP EQUATION MULTIPLIED BY 2.00

LENGTH      HEAT DUTY      PRESSURE,      TEMPERATURE      DELTA T       REYNOLDS NO.      OVERALL U
  FT.        BTU/HR         IN. HG         DEG. F.         DEG. F.                       BTU/HR FT2 F

  2.00       1882984.       3.72351        125.29          10.856          1551.            312.50
  4.00       3715908.       3.75297        125.54          10.588          1578.            311.94
  6.00       5507279.       3.77855        125.74          10.360          1603.            311.58
  8.00       7264933.       3.80049        125.92          10.170          1628.            311.44
 10.00       8996418.       3.81903        126.06          10.014          1652.            311.58
 12.00      10709192.       3.83437        126.16           9.890          1676.            312.07
 14.00      12410904.       3.84674        126.24           9.796          1699.            313.03
 16.00      14109810.       3.85632        126.30           9.730          1722.            314.64
 18.00      15815570.       3.86335        126.33           9.689          1744.            317.24
 20.00      17540989.       3.86805        126.33           9.672          1767.            321.48
 22.00      19307415.       3.87068        126.32           9.677          1789.            328.97
 24.00      21171409.       3.87164        126.28           9.701          1812.            346.28

             HRI PROGRAM FOR LTV EVAPORATOR HEAT TRANSFER CALCULATIONS

          PROJECT    21,700  -  DOW CHEMICAL COMPANY  -  OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200      TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.      EFFECT NO. 12

TRIAL NUMBER    6     TUBE NUMBER   533.            PRESSURE DROP EQUATION MULTIPLIED BY 2.00

LENGTH      HEAT DUTY      PRESSURE,      TEMPERATURE      DELTA T       REYNOLDS NO.      OVERALL U
  FT.        BTU/HR         IN. HG         DEG. F.         DEG. F.                       BTU/HR FT2 F

  2.00       1893257.       3.72317        125.29          10.857          1542.            312.36
  4.00       3736732.       3.75230        125.53          10.593          1569.            311.81
  6.00       5539087.       3.77757        125.73          10.369          1594.            311.46
  8.00       7308181.       3.79923        125.90          10.181          1619.            311.34
 10.00       9051597.       3.81749        126.04          10.028          1643.            311.50
 12.00      10776853.       3.83258        126.15           9.907          1667.            312.03
 14.00      12491686.       3.84470        126.22           9.816          1690.            313.03
 16.00      14204503.       3.85407        126.27           9.752          1713.            314.71
 18.00      15925224.       3.86089        126.30           9.714          1735.            317.41
 20.00      17667198.       3.86540        126.30           9.699          1758.            321.84
 22.00      19453571.       3.86787        126.29           9.706          1780.            329.78
 24.00      21344185.       3.86870        126.25           9.732          1804.            348.05
```

SAMPLE OUTPUT (Continued - 3)

```
          PROJECT   21,700  -  DOW CHEMICAL COMPANY  -  OSW FREEPORT PLANT EXPANSION

RUN NUMBER  1200      TUBE LENGTH= 24.0 FT.     TUBE DIAMETER= 2.000 INCHES O.D.     EFFECT NO. 12

HEAT DUTY          OVERALL U          TOTAL AREA        TUBE       PRESSURE DROP       DELTA T.
 BTU/HR          BTU/HR FT2 F           SQ. FT.        NUMBER           IN. HG.          DEG. F

21344185.          312.4 'BTM           6697.89         533.0        0.178804249       10.86 -BTM
                   348.0 -TOP                                                           9.73 -TOP



                  CALCULATED FEED CONDITIONS AT TUBE INLET FOR COMPARISON


FEED RATE      FEED TEMP.     FEED LIQUID     FEED VAPOR      STEAM CHEST      TUBE INLET      TUBE INLET
 LBS/HR         DEG. F          LBS/HR          LBS/HR       PRES. IN. HG    PRES. IN. HG   TEMP. DEG. F

189660.        138.0000        189248.          412.3         3.74360          3.86870        126.25067



                                     PROGRAM INPUT DATA

    21700       1200          12   24.00000    2.00000    1.90200 21320000.          0
 138.0000   125.0000     189660.     21506.    168154. 136.00000    1.65770    3.74360
1016.4000   120.0000      3.4458   165.0000    10.8630   58.0000     0.3565     2.5000
  2.00000    0.02660    66.39400    0.89500    0.38450   1.00000    0.42000   61.40000
500.00000    2.00000     1.00000    1.00000          1   2.000000.00125000
```

Program Nomenclature:

A. Input Data

1.	JOB - Job Number	
2.	IRUN - Run Number	
3.	IEFECT - Effect Number	
4.	TL - Tube Length	Ft.
5.	DIAO - Outside Tube Diameter	Inches
6.	D - Inside Tube Diameter	Inches
7.	QS - Total Heat Duty	Btu/Hr.
8.	INUM - a(1) in Column 80 - means skip property data read in-Items 9 to 32	
9.	TF - Feed Temperature	°F.
10.	T2 - Tube Bottom Temperature	°F.
11.	WF - Total Feed Rate	lbs/Hr.
12.	V2 - Total Vapor from Unit	lbs/Hr.
13.	W2 - Total Liquid from Unit	lbs/Hr.
14.	TS - Temperature of Steam	°F.
15.	UL2 - Viscosity of Liquid @ BTM	$\frac{\text{lb.-mass}}{\text{ft. hr.}}$
16.	PS - Steam Pressure	in. Hg.
17.	FLAMS - Latent Heat of Steam	BTU/#
18.	TR1 - Reference Temperature @ 1	°F.
19.	PR1 - Reference Pressure @ 1	in Hg.
20.	TR2 - Reference Temperature @ 2	°F.

21.	PR2 - Reference Pressure @ 2	in. Hg.
22.	TKT - Thermal Conductivity of Tube	$\frac{\text{Btu-ft.}}{\text{Hr(Ft.}^{2}\text{)°F.}}$
23.	TKL - Thermal Conductivity of Saline	$\frac{\text{Btu-ft.}}{\text{Hr(Ft}^{2}\text{)°F.}}$
24.	BPRO - Boiling Point Rise at BTM1	°F.
25.	BPRI - Boiling Point Rise at Inlet	°F.
26.	UG - Viscosity of Steam	lbs mass/ft.hr.
27.	ROL - Density of Saline	lbs/ft.^{3}
28.	CPL - Heat Capacity of Saline	Btu/lb.°F.
29.	TKS - Thermal Conductivity of Water	$\frac{\text{Btu/ft.}}{\text{Hr.(ft}^{2}\text{)°F.}}$
30.	CPS - Heat Capacity of Water	Btu/lb.°F.
31.	CPV - Heat Capacity of Steam	Btu/lb.°F.
32.	ROLS - Density of Water @ T	lbs/ft.^{3}
33.	UC - Overall Coefficient-1st Assumption	$\frac{\text{Btu}}{\text{Hr(Ft}^{2}\text{)°F.}}$
34.	XDP - Pressure Drop Convergence Parameter	
35.	XTN - Tube Number Convergence Parameter	
36.	XQN - Heat Duty Convergence Parameter	
37.	IRN - Reynolds Number Directive	
38.	DL - Incremental Tube Length	Ft.
39.	RD - Fouling Factor	

B. Nomenclature of Fortran IV Statements Internal to Program Listing

1. CC - Clausius Clapeyron type constant
2. ABETA - Constant in Beta equation
3. ADP - Constant in pressure drop eq.
4. RELC - Reynolds Number eq. constant - saline
5. RESC - Reynolds Number eq. constant - water
6. RW - Resistance of tube wall to heat transfer
7. ULC - Constant in viscosity equation
8. REL - Reynolds Number on saline side
9. RES - Reynolds Number on steam side
10. PRL - Prandtl Number on saline side
11. PRS - Prandtl Number on steam side
12. Q - Accumulating register for heat transferred
13. W - Accumulating register for vaporized material
14. V - Accumulating register for flashing material
15. DQ - Incremental heat transfer from steam side
16. DW - Incremental water vaporized on saline side
17. DV - Incremental flashing of liquid in tube
18. TLX - Tube length register from Btm to Point X.
19. ROG - Density of vapor
20. ROL - Density of liquid saline
21. DTA - Avg. temperature drop from saline to steam side
22. H1 & H2 - Nusselt Number from graphical data.

23. HXA - heat transfer coefficient for increment - saline side
24. HSA - heat transfer coefficient for increment - steam side
25. UCA - overall coefficient calculated for increment
26. DP - Two phase pressure drop
27. PX - Point pressure at point X
28. TX - Temperature @ point X
29. TXS - Temperature @ point X saturated
30. TN - Tube number
31. TNI - Tube number - Initial assumption

REFERENCES

1. Dukler, A. E., "Fluid Mechanics and Heat Transfer in Vertical Falling-Film Systems", Chemical Engineering Symposium Series 30, Vol. 56, p. 1-10, 1960

2. Prengle, Dukler & Crump, Inc., "Heat Transfer in the LTV Evaporator - An Analysis of Pilot Plant Data and Predictive Techniques for Plant Operation and Design", Saline Water Research and Development Progress Report No. 74. (PB 181 484) June 1963

3. IBM Systems Reference Library, IBM 7090/7094 Programming Systems, Fortran IV Language, Form C28-6274-1 , 1963

4. IBM Systems Reference Library, IBM 7090/7094 IBSYS Operating System, IBJOB Processor, Form C28-6275-2, 1963

RESULTS AND ANALYSIS

Table I summarizes most of the final computer calculations. Included in this table are the results of the study to determine the influence of tube diameter and length and to evaluate the influence of recirculation rate on the number of tubes required. These results are summarized graphically in Figures 1 & 2 for Effect No. 1; Figures 3 & 4 for the 8th Effect; and in Figures 5 & 6 for the 12th Effect. All of these cases were executed for tube spacings in 1.25 times the tube diameter. For such a spacing pressure drop on the tube side is negligible and the heat transfer coefficient on that side is dictated only by the amount of condensate flowing.

Result of Changing Tube Diameter and Length on Area Requirements: The most dramatic influence of tube diameter and length appear in the 12th effect and can be seen in Figures 5 & 6. Currently 2" - 24 foot long tubes are in use. Changing to larger diameter tubes or shortening tubes causes a marked lowering in surface area required. At larger tube sizes the effect of tube length becomes less important. It seems clear that there is a large immediate advantage to increasing tube size to 3 to 4 inch. The reason for this is clear. In the twelfth effect, two inch tubes cause excessive pressure gradient, thus decreasing the mean tempera-

TABLE I

21,700 - HRI PROGRAM FOR LTV EVAPORATOR HEAT TRANSFER CALCULATIONS
SUMMARY OF RESULTS

TUBE SIZE	EFFECT NO. I				
O.D. 16 BWG	RUN NO.	TUBE LENGTH·FT	TUBE NUMBER	TOTAL AREA·FT²	ΔP IN. Hg
3/4"	107	20'	1776	6974	1.423
"	108	24'	1571	7403	2.401
"	109	30'	1389	8182	2.979
1"	101	20'	1245	6519	.5628
"	102	24'	1063	6679	.8769
"	103	30'	892	7006	1.446
2"	104	20'	611	6398	.0535
	105	24'	509	6396	.0886
	106	30'	408	6409	.1630
100%	111	24'	498	6258	.1220
200%	121	24'	493	6195	.1446
300%	131	24'	490	6158	.1642
3"	112	24'	340	6409	.0236
	113	30'	271	6385	.0442
	110	20'	409	6425	.0142
4"	114	20'	308	6451	.0056
	115	24'	256	6434	.0094
	116	30'	204	6408	.0176

TUBE SIZE	EFFECT NO. VIII				
O.D. 16 BWG	RUN NO.	TUBE LENGTH·FT	TUBE NUMBER	TUBE AREA·FT²	ΔP IN. Hg
1"	802	20'	1411	7388	.7672
"	801	24'	1296	8143	1.018
"	803	30'	1203	9448	1.343
1¼"	817	8'	2373	6213	.0408
	818	12'	1584	6220	.1247
	819	16'	1218	6377	.2605
	820	20'	1020	6676	.4345
	821	24'	901	7076	.6304
	822	30'	800	7854	.9221
2"	808	8'	1493	6254	.0081
	807	12'	989	6214	.0254
	806	16'	741	6208	.0564
	804	20'	595	6230	.1036
	888	24'	500	6283	.1680
	805	30'	411	6456	.2917
3"	812	8'	998	6270	.0022
	811	12'	664	6258	.0067
	810	16'	497	6245	.0149
	809	20'	396	6220	.028
4"	816	8'	749	6276	.0009
	815	12'	500	6283	.0027
	814	16'	374	6266	.0060
	813	20'	299	6262	.0111

TUBE SIZE	EFFECT NO. XII				
O.D. 16 BWG	RUN NO.	TUBE LENGTH	TUBE NUMBER	TOTAL AREA·FT²	ΔP IN. Hg
2"	1204	8'	1495	6262	.0108
	1203	12'	1001	6289	.0331
	1202	16'	762	6384	.0709
	1201	20'	626	6555	.1237
	1200	24'	542	6811	.1876
100%	991	24'	578	7263	.2473
200%	992	24'	582	7314	.2769
300%	993	24'	585	7351	.2959
3"	1208	8'	996	6258	.0029
	1207	12'	663	6249	.0090
	1206	16'	499	6271	.0198
	1205	20'	401	6299	.0365
4"	1212	8'	747	6258	.0149
	1211	12'	498	6258	.0080
	1210	16'	373	6250	.0036
	1209	20'	299	6262	.0012

ture driving force more than the heat transfer coefficient is increased. Increasing the tube size reduces the gradient. This is most marked in the high vacuum effect because the vaporizing coefficient in the tube is significantly smaller than the condensing coefficient outside. Of course, any economic advantage depends on the effect of increasing tube size on capital costs. This can be determined only through a cost analysis.

Trends for the first effect are similar to those in the twelfth. As tube diameter is increased and tube length shortened the area required decreases. However, where the minimum for Effect 12 seems to fall at about 4 inch diameter, the first effect minimum appears to be about 2". It is expected that in the first effect, smaller tubes would show improved transfer. This was not the case. Supplementary calculations revealed that no advantage could be taken of the smaller tubes because at this high pressure and with wide spacing between tubes the shell side coefficient was controlling. Thus, as tube diameter is decreased the coefficient inside the tube increases, but this is more than offset by lower coefficient on the shell side due to lower per tube Reynolds number. This points clearly to a way to increase performance on the shell side in the first effect. If some of the free areas on the shell side could be restricted, thus causing measurable pressure drop, the shell side coefficient which is now controlling could be increased This it would be possible to take advantage of smaller tube

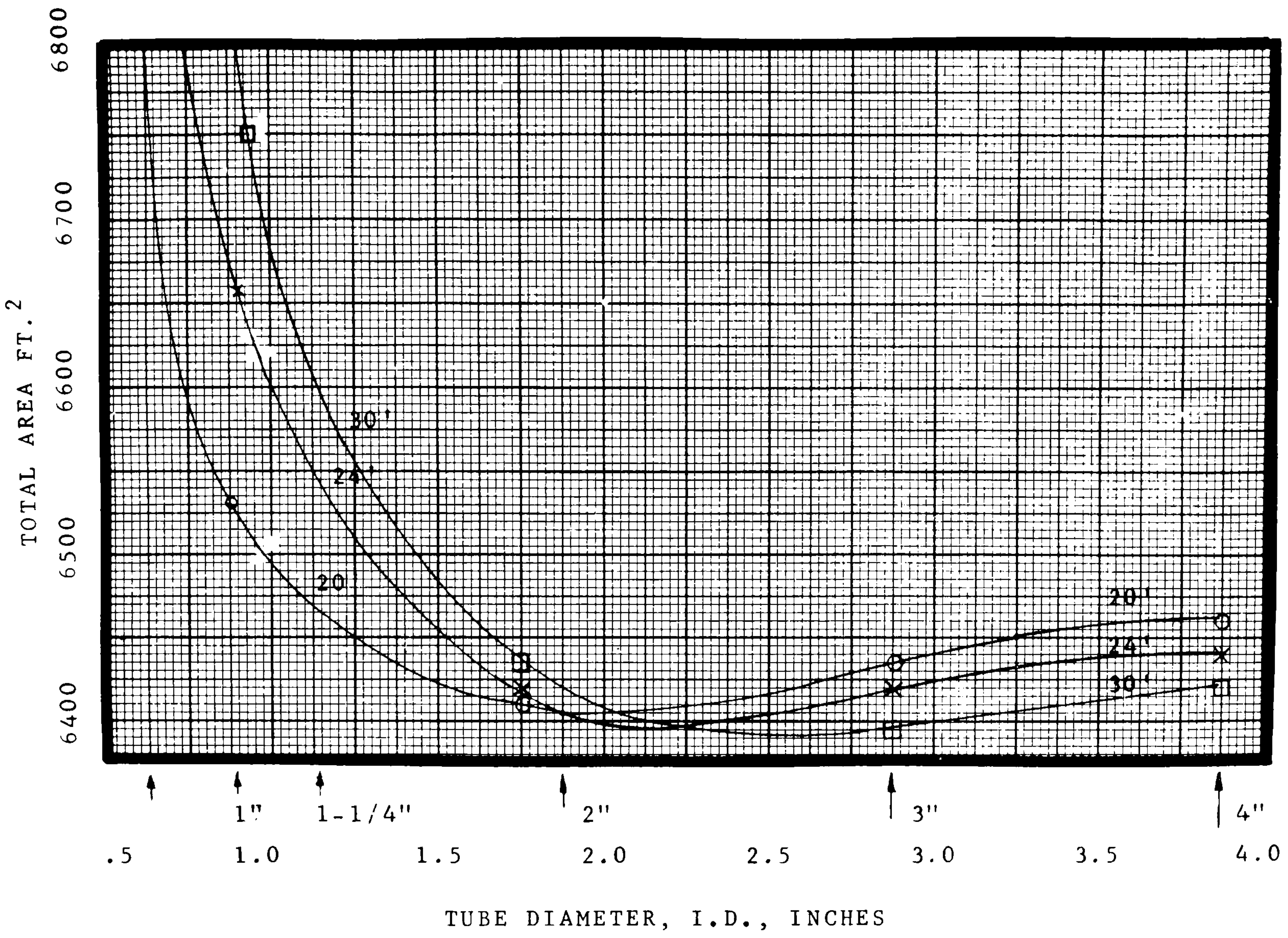


FIGURE 2

TOTAL AREA VS TUBE DIAMETER
EFFECT NO. I

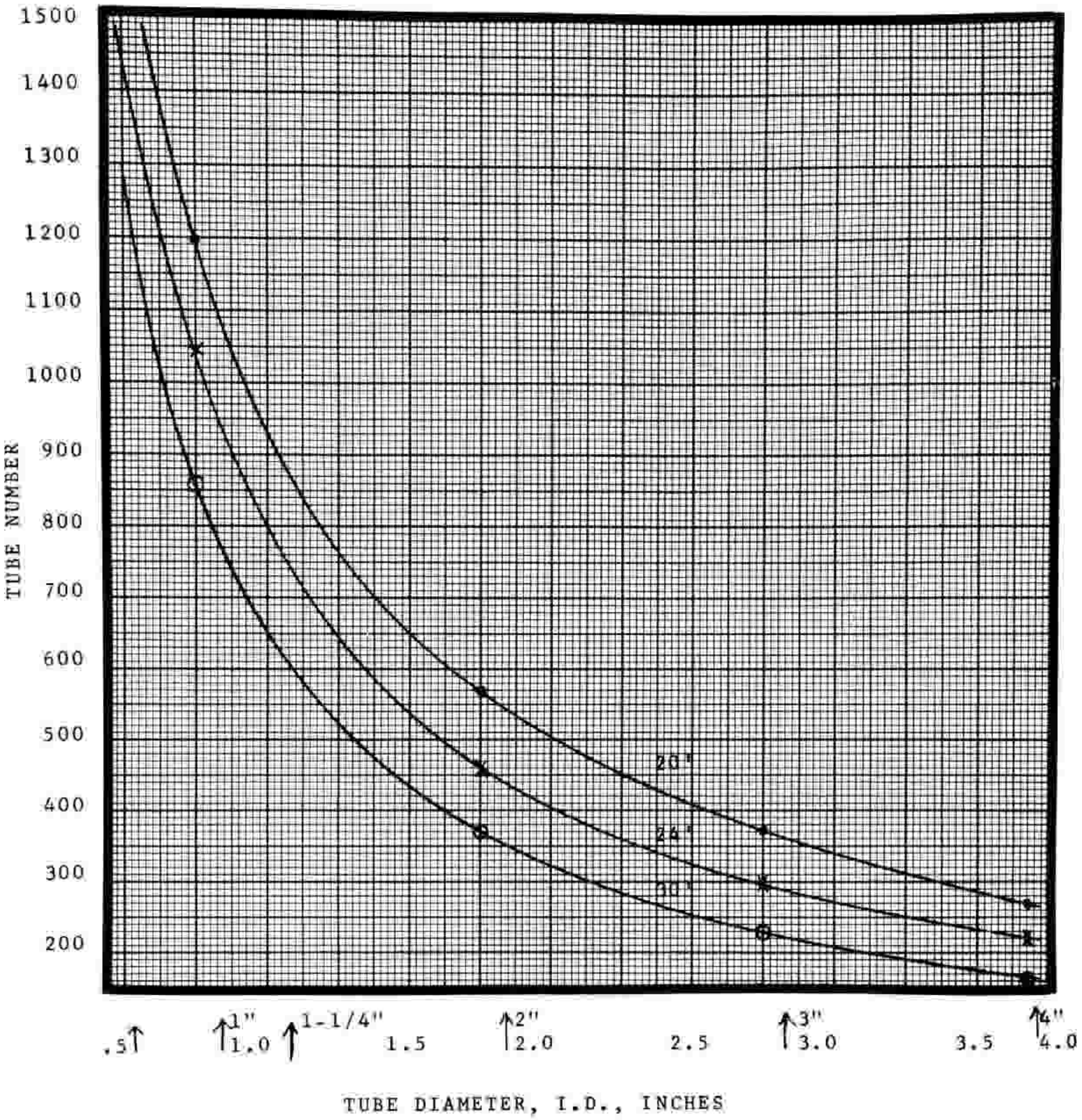


FIGURE 3
TUBE NUMBER VS TUBE DIAMETER
EFFECT NO. I

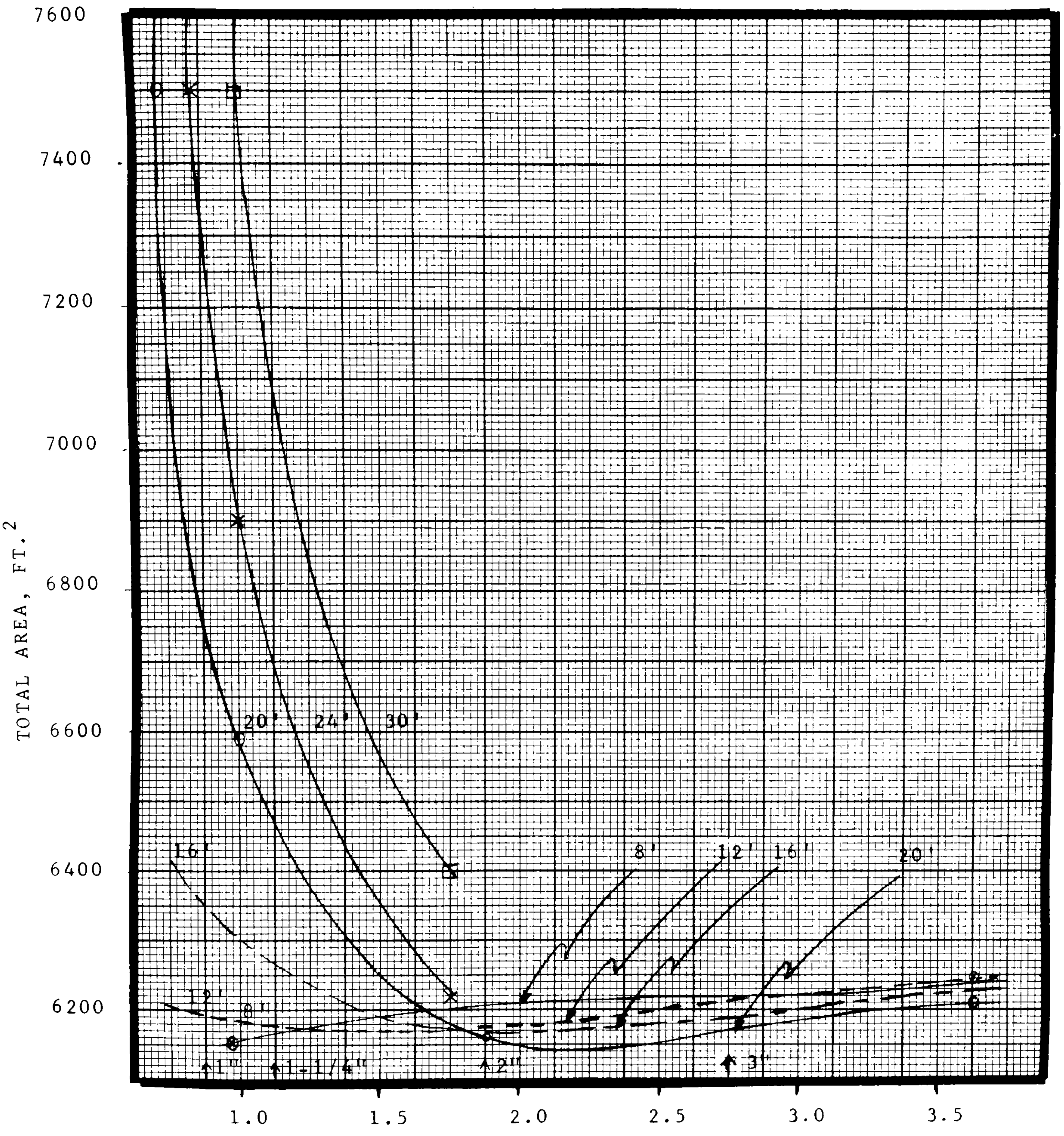


FIGURE 4

TOTAL AREA VS TUBE DIAMETER
EFFECT NO. VIII

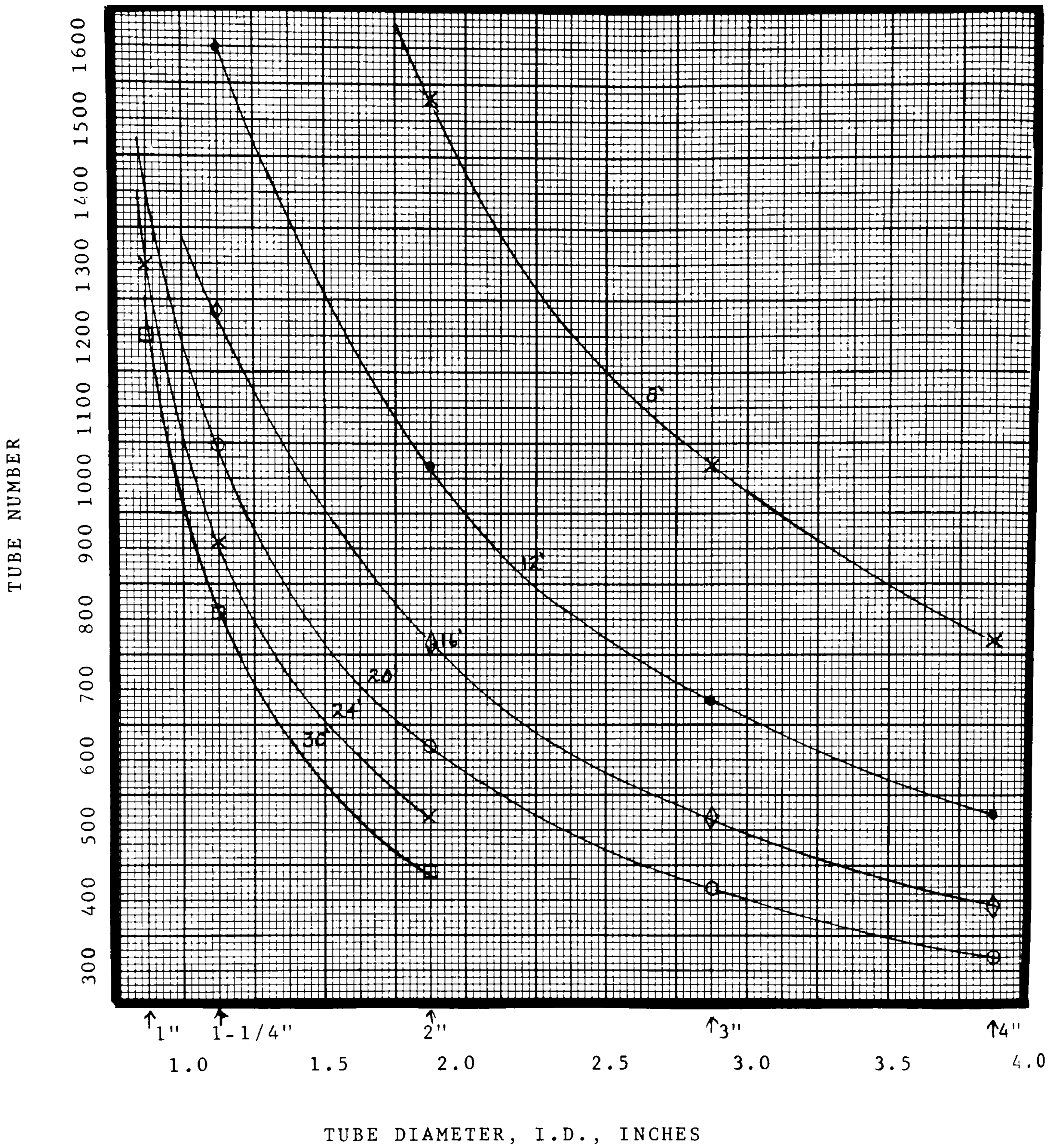


FIGURE 5

TUBE NUMBER VS TUBE DIAMETER
EFFECT NO. VIII

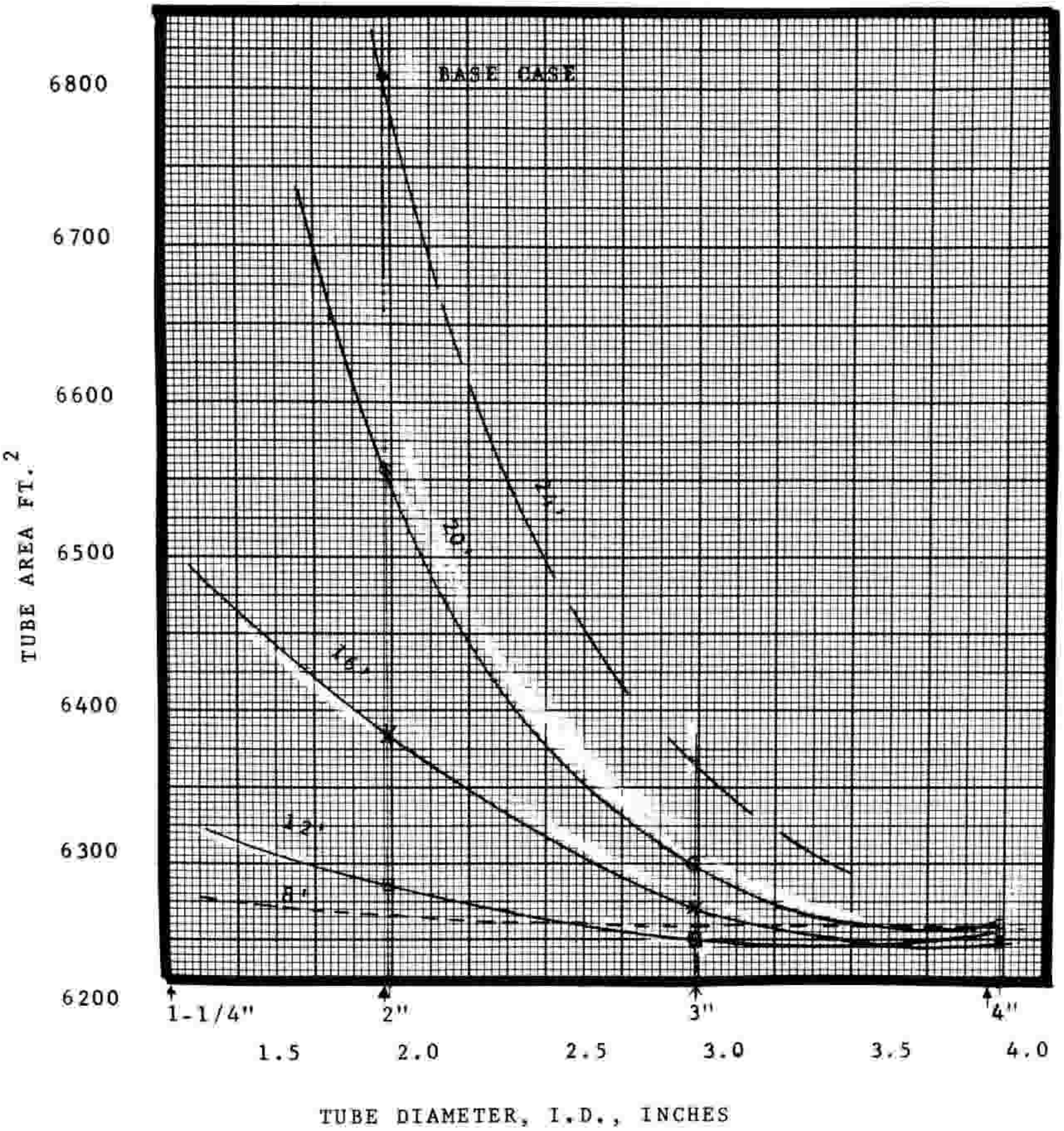


FIGURE 6

TOTAL AREA VS TUBE DIAMETER
EFFECT NO. XII

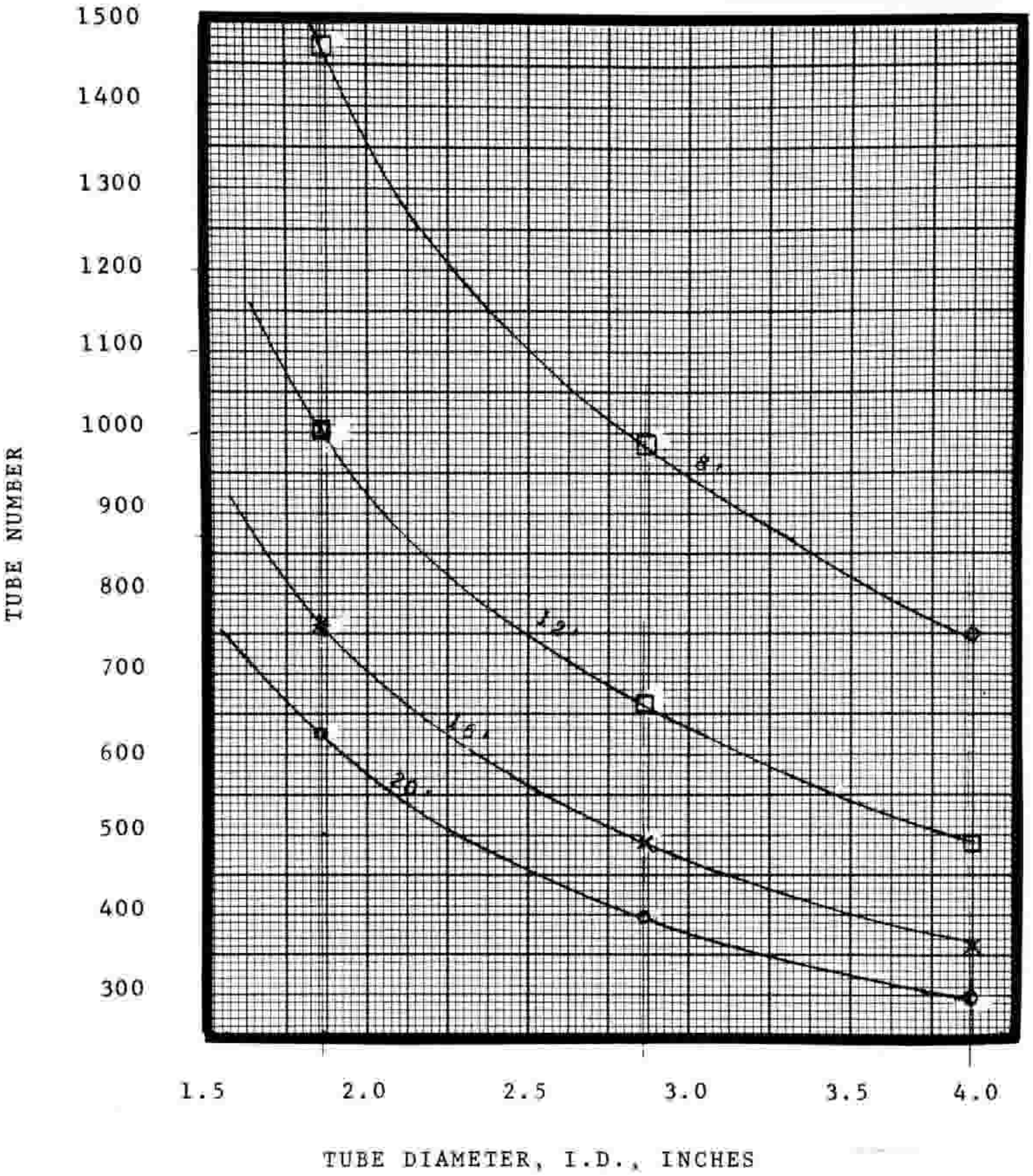


FIGURE 7

TUBE NUMBER VS TUBE DIAMETER
EFFECT NO. XII

sizes to decrease the area required still more.

__Result__ __of__ __Recirculation__ __on__ __Area__ __Requirement__: Recirculation studies were made on the first and twelfth effects. In each case the tube dimensions were fixed at 2.0 inch diameter and 24 ft. long and the effect of recirculation on tube number requirements calculated. The result of recirculation in these two effects are summarized below.

Recirculation	Area Required Effect 1	 Effect 12
0	6396 sq.ft.	6811 sq.ft.
100%	6258	7263
200%	6195	7314
300%	6158	7351

Note the inverted effect of recirculation between Effects 1 and 12. In Effect 1, recirculation decreases the area required, in Effect 12 the result is an increased area. This is perfectly reasonable. Recirculation tends to decrease the sensible heat required to heat the feed and thus utilize more of the energy transferred in latent heat. It does this at the expense of increased flow rate and pressure drop in the tube. In the first effect the increased shear actually increases the coefficient with negligible temperature drop. In the twelfth effect the increased pressure drop is more than offset by a decreased temperature driving force and the net result is a lower heat flux.

Result of Mal-Distribution on Area Requirements: In order to evaluate the effect of mal distribution on the area required, extensive computer runs were made for conditions of the first and twelfth effect. The tubes in each effect were divided into three zones and the liquid flow increased in one zone, kept at normal in the second and decreased in the third to meet total flow requirements. Results are summarized below for the case of 2", 24 ft. long tubes.

Effect	Normal Dist	TOTAL NO. TUBES REQUIRED 120/100/80	TOTAL NO. TUBES REQUIRED 150/100/50
1	509	510	512
12	542	543	544

The influence of mal distribution on tube numbers is thus seen to be negligible. It should be noted that such calculations assume that the tubes remain wetted in the liquid deficient region and that the coefficient does not change due to sudden scaling of the surfaces.

Influence of Mal-Distribution on Local Concentrations: Despite the fact that mal-distribution of the feed does not appear to seriously affect the area requirements it can be undesirable because of the high local concentrations. The relative insensitivity of heat flux to mal distribution means that a tube with low flow will transfer about the same amount of heat and vaporize the same amount as the tube with normal

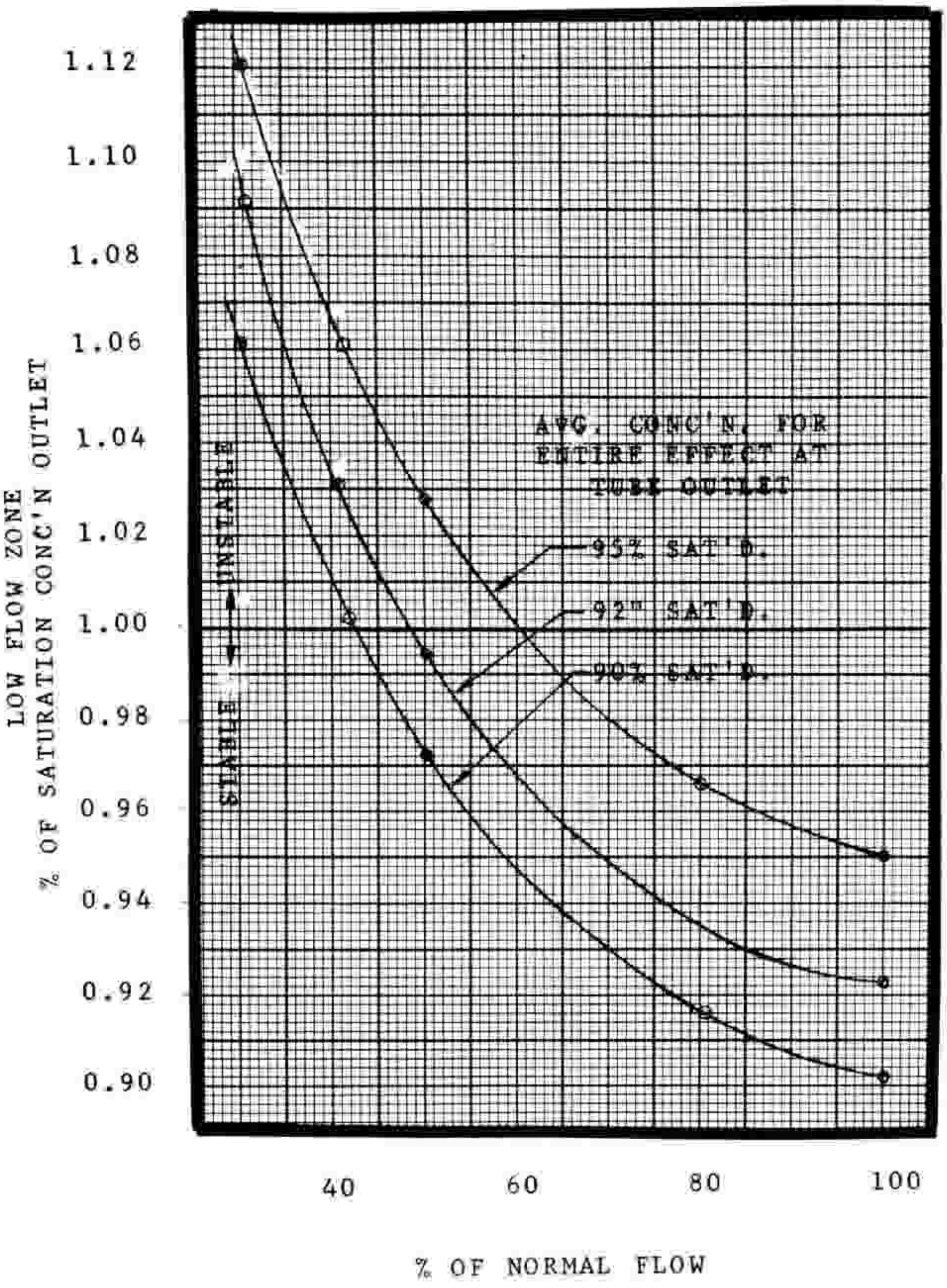


FIGURE 8

EFFECT OF MAL-DISTRIBUTION
ON LOCAL CONCENTRATION
EFFECT NO. 1

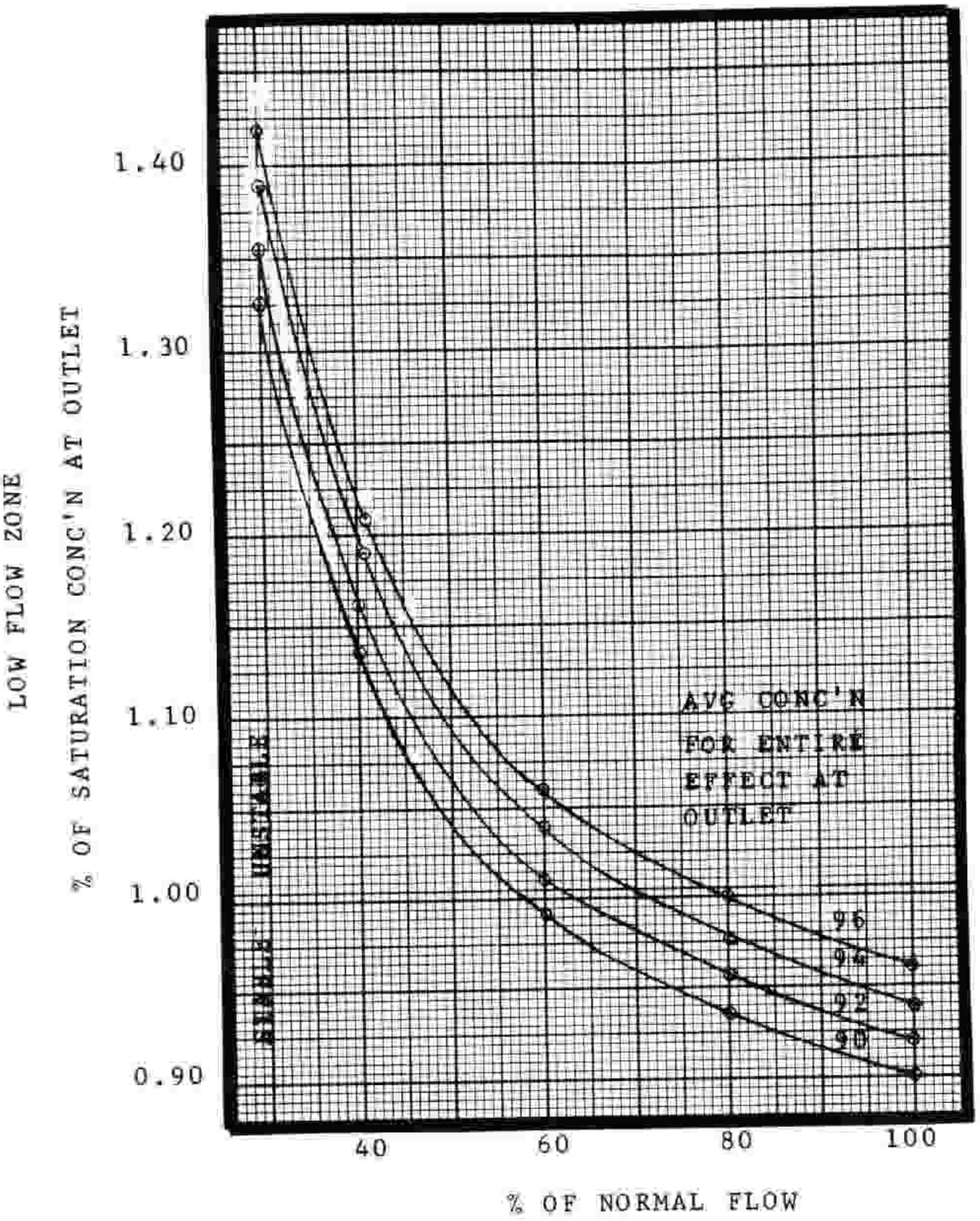


FIGURE 9

EFFECT OF MAL-DISTRIBUTION
ON LOCAL CONCENTRATION
EFFECT NO. 12

flow. Thus, the liquid leaving low flow tube is of a higher concentration than those with normal or excess flow. When this local concentration exceeds the saturation concentration at the temperature in the effect scaling can occur. In an effect operating with part of the tubes at a low liquid rate, even though the average concentration in the sump is well below saturation the liquid deficient tubes can be scaling. Calculations were made to demonstrate this behavior, and the results appear as Figures 7 and 8. Each curve represents the average concentration (relative to saturation) in the sump. As the local flow rate in a tube (as expressed by percent of normal flow on the abscissa) drops the local concentration (expressed as percent of saturation concentration on the ordinate) increases. Thus in Figure 7, if the liquid in the sump is at 95% of saturation, then when the liquid flow in any one tube drops below 60% of normal, the concentration leaving that tube will be above saturation and scaling can be expected. Because of operating conditions, Effect 12 is much more subject to this behavior. The rather small mal distribution can cause local concentrations to exceed saturation.

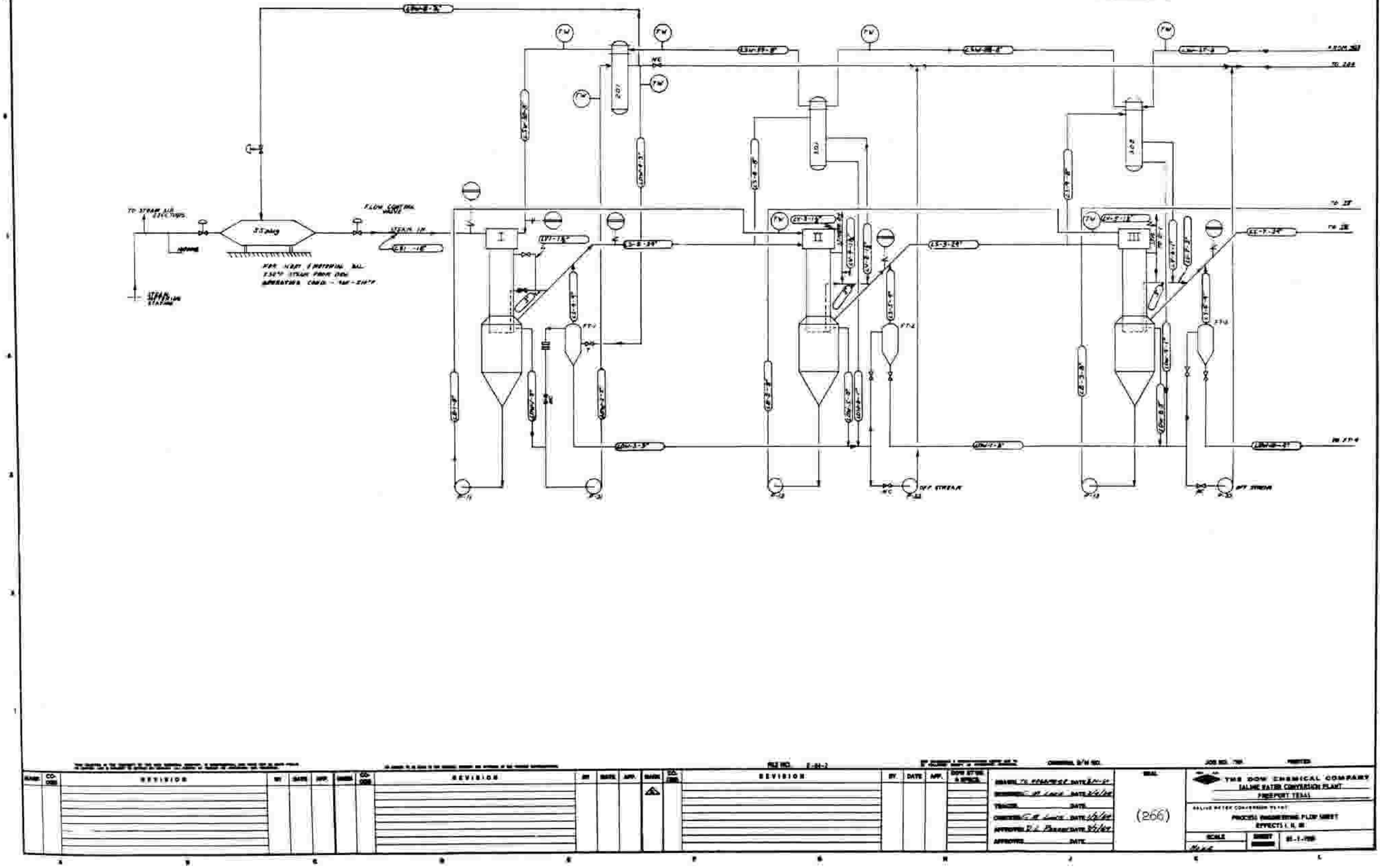
One of the benefits of recirculation can be seen from these calculations. Where an effect operates near saturation in the sump liquid, recirculation will help prevent local scaling since it will tend to minimize local mal distributions. In addition, the larger flow rate at the same heat transfer rate results in a smaller concentration change across the tube, as shown above. However, this can be attained only at the price of increased area.

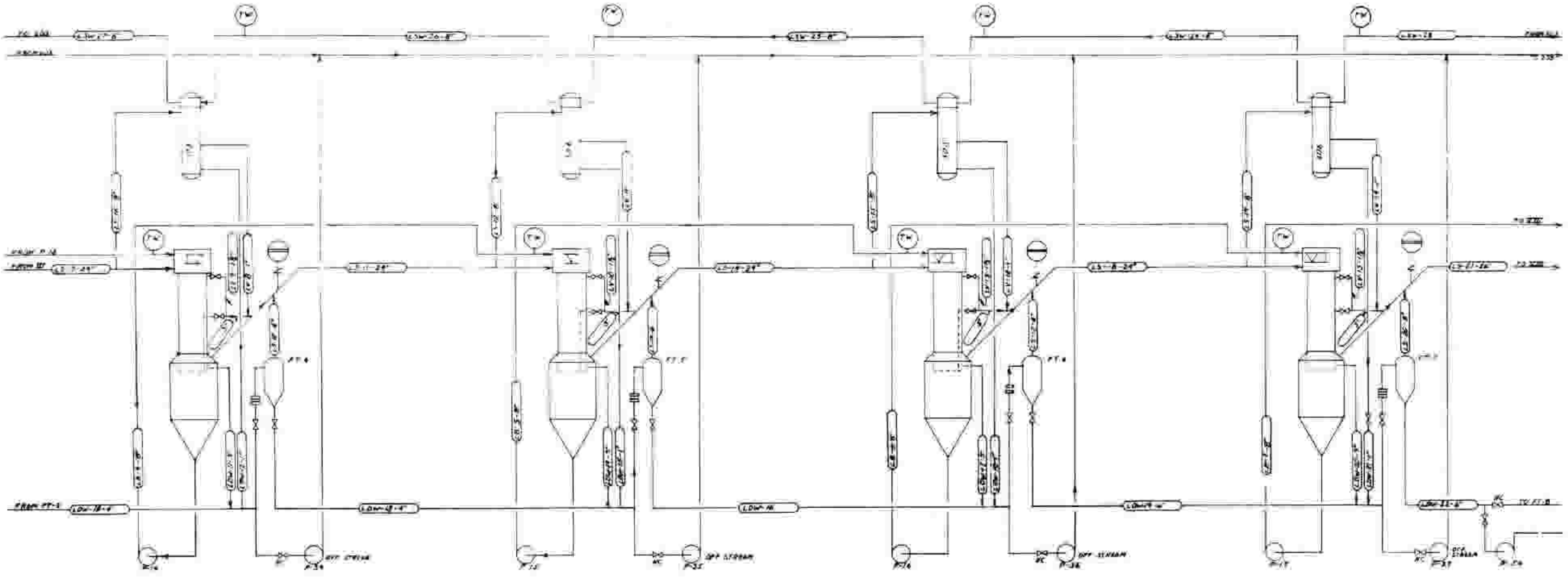
Influence on Closer Tube Spring on Area Required: As modifications are made to increase heat transfer on the tube side, transfer rate on the condensing side quickly becomes limiting. In fact, as discussed above, changes in the tube geometry for the first effect is of no value because shell side coefficient is, in fact, already limiting. One way to increase this condensing coefficient is to cause significant pressure drop to take place due to gas shear across the condensate interface. One way to do this is to decrease the flow area on the tube side by using closer tube spacing. Calculations were made to determine if significant condensate side shear could be introduced by the following modified spacings:

2" tube on 2-3/8" triangular pitch
3" tube on 3-1/2" triangular pitch
4" tube on 4-1/2" triangular pitch

These calculations indicated that the increased shear due to smaller spacing is negligible. Still more closely spaced tubes would introduce problems in web strength on the tube sheets. Thus the only alternative is to block off additional area using blank inserts between tube sheets on the shell side. This study was not pursued further.

APPENDIX B


TO STEAM AIR EJECTORS
STEAM SUPPLY LINE STATION
35 psig
FOR HEAT & MATERIAL BAL.
350°F STEAM FROM DOW
OPERATING COND. - 150° - 310°F
FLOW CONTROL VALVE
STEAM IN
I
II
III
201
202
203
FT-1
FT-2
FT-3
TW
P-11
P-12
P-13
P-21
P-22
P-23
OFF STREAM
FROM 303
TO 303
TO IV
TO FT-4
THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS
SALINE WATER CONVERSION PLANT
PROCESS ENGINEERING FLOW SHEET
EFFECTS I, II, III
REVISION
DRAWN
CHECKED
APPROVED
DATE
SCALE
SHEET
FILE NO.
JOB NO.



FILE NO. F-64-2

ORIGINAL D/S NO.

DRAWN	DATE
DESIGNED G. M. Lewis	DATE
TRACED	DATE
CHECKED	DATE
APPROVED D. L.	DATE
APPROVED	DATE

SEAL

(267)

JOB NO.

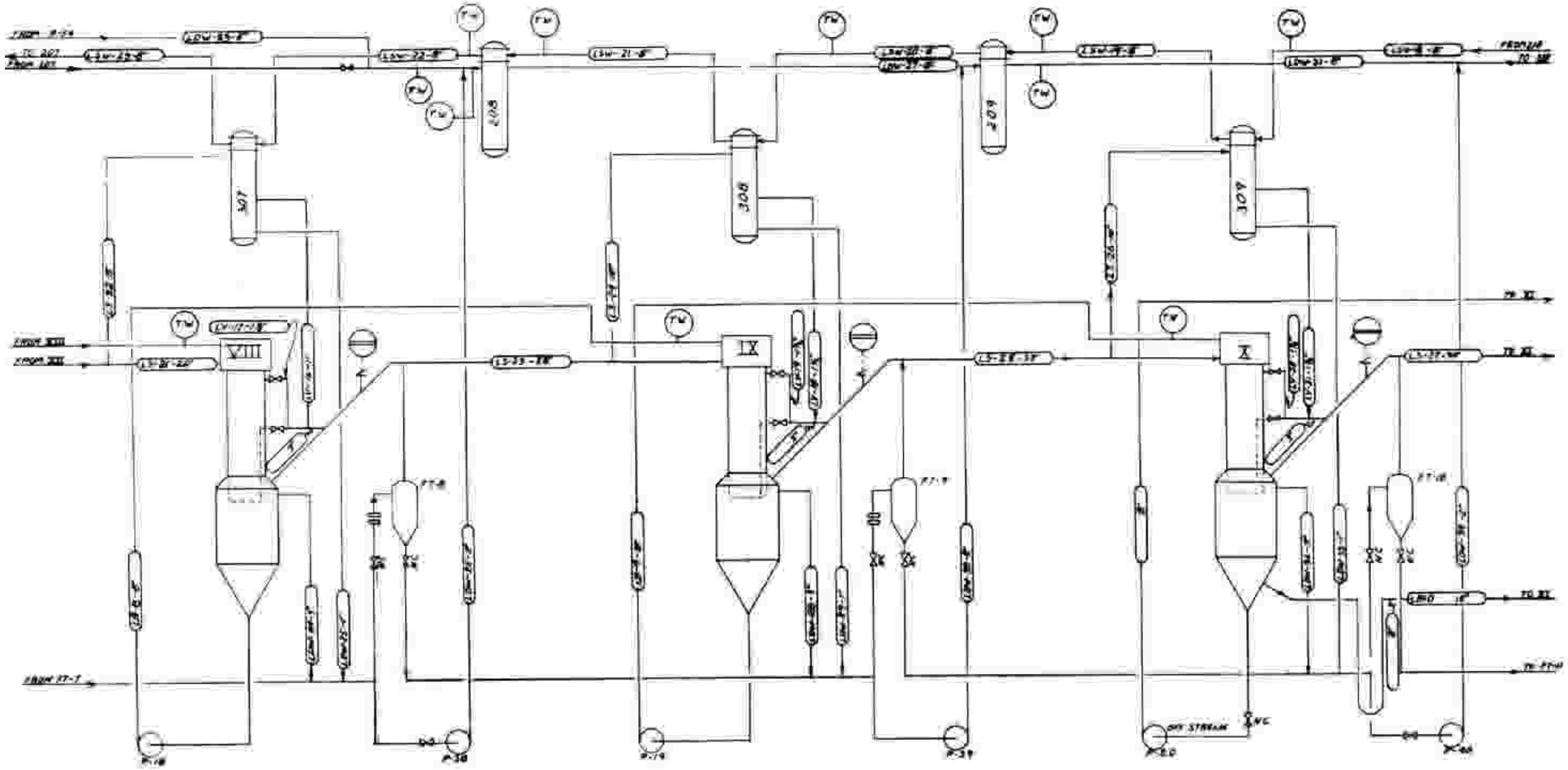
PRINTED

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS

SALINE WATER CONVERSION PLANT
PROCESS ENGINEERING FLOW SHEET
EFFECTS IV, V, VI, VII

SCALE	SHEET NUMBER	
None		

MARK	CO-ORD	REVISION	BY	DATE	APP.



FILE NO. F-66-2

ORIGINAL D/N NO.

JOB NO. 7301

PRINTED

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NAME	CO-ORD.	REVISION	BY	DATE	APP.

NAME	CO-ORD.	REVISION	BY	DATE	APP.

DESIGNED DATE

DRAWN DATE

TRACED DATE

CHECKED C.M. Lowe DATE

APPROVED DATE

APPROVED DATE

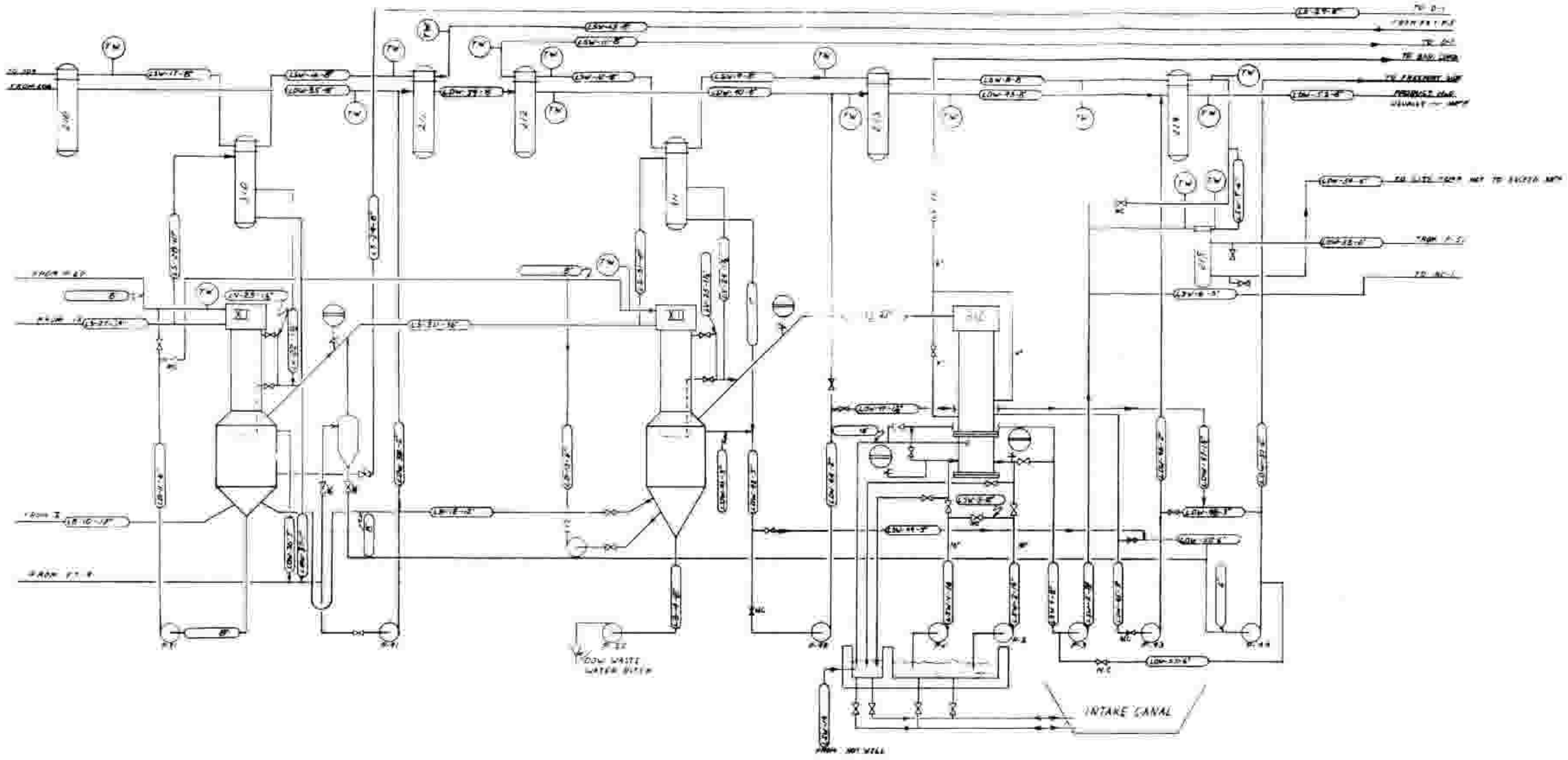
(268)

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT, TEXAS

SALINE WATER CONVERSION PLANT
PROCESS ENGINEERING FLOW SHEET
EFFECTS VIII, IX, X

SCALE None

SHEET NUMBER



Ref. No. F-26-1

JOB NO. 7561

DRAWN: C.L. Kilcrease DATE

DESIGNED: C.E. Lake DATE

TRACED: DATE

CHECKED: C.E. Lake DATE

APPROVED: D.L. Peterson DATE

APPROVED: DATE

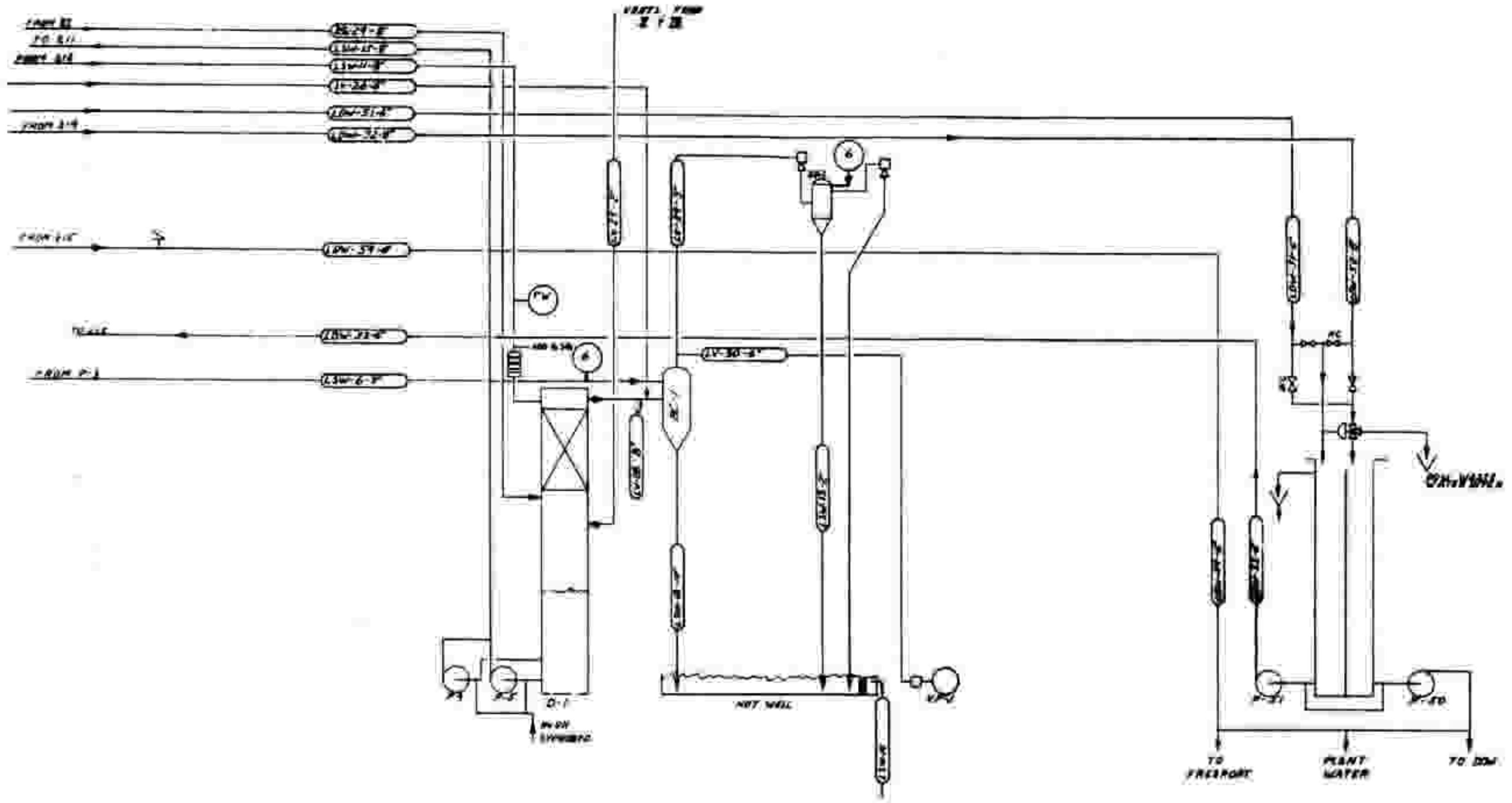
(269)

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS

SALINE WATER CONVERSION PLANT
PROCESS ENGINEERING FLOW SHEET
EFFECTS XI, XII

SCALE: NONE

SHEET



MARK	CO. ORD.	REVISION	BY	DATE	APP.	MARK	CO. ORD.	REVISION	BY	DATE	APP.	MARK	CO. ORD.	REVISION	BY	DATE	APP.	DOW STD'S. & SPECS.

ORIGINAL S/D NO.

DRAWN BY DATE
TRACED DATE
CHECKED DATE
APPROVED DATE
APPROVED DATE

SEAL

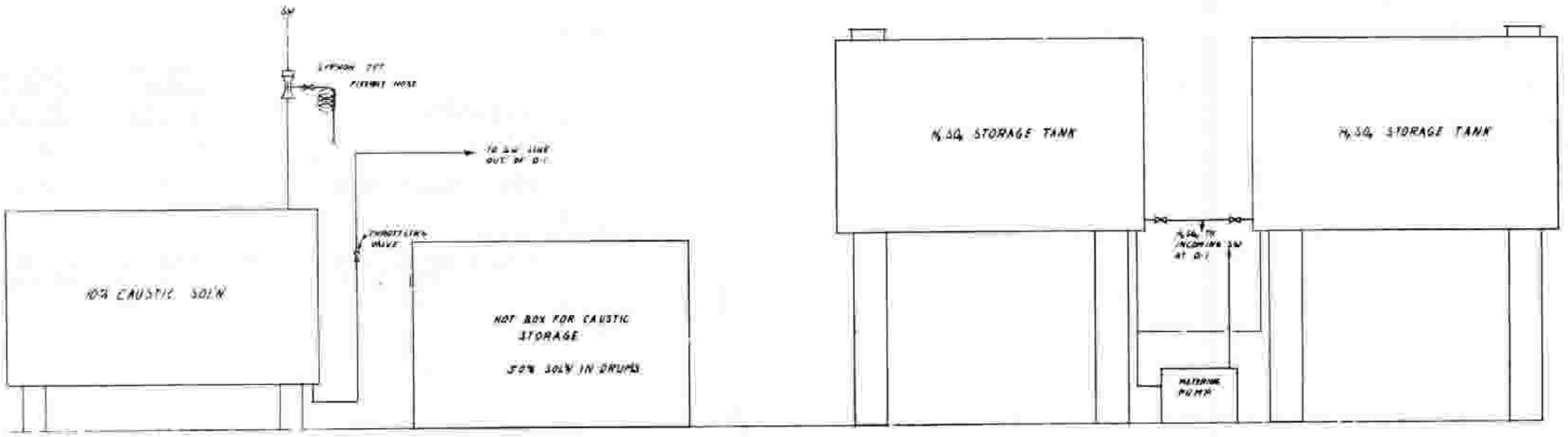
(270)

JOB NO. 7301

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS

PROCESS ENGINEERING FLOW SHEET
DEAERATOR AND PRODUCT DISTRIBUTION

SCALE None
SHEET NUMBER 61-A-708



REVISION

REVISION

FILE NO. F-44-1

REVISION

(271)

THE DOW CHEMICAL COMPANY
SALINE WATER CONVERSION PLANT
FREEPORT TEXAS

PROCESS ENGINEERING FLOWSHEET
CHEMICAL

SCALE None

7180

APPENDIX C

P. E. Muehlberg (2)

THE DOW CHEMICAL COMPANY
TEXAS DIVISION
CENTRAL LABORATORY FREEPORT

FILE 40206
DATE THIS REPORT 4-13-64
CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION

DATE OF SAMPLE 4-10-64

Sample No.	Raw Sea Water No. 1	Down Stream from Deaerator No. 2	Up Stream afte Acidification No. 3
PPM CO_2	92	2.8	68
PPM Dissolved Oxygen	6.5	0.01	4.2

Note - Accuracy of the results shown on deaerated seawater (sample No. 2) is probably no better than ± 50% of the amounts reported.

BY: JBH and LTJ jsm

SIGNED E. K. Hill

7180

DOW

P. Muehlberg

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE

DATE THIS REPORT 6-11-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Deaerator Samples - Saline Water Plant

DATE OF SAMPLE

Sample	PPM Oxygen	PPM CO_2
Feed	3.6	40
Effluent	<0.005	3.6
Vapor	(Poor Sample)	1300
No. 11 Steam	None detected	None detected
No. 2 Steam	None detected	None detected

BY: RHD jsm

SIGNED R H D[illegible]

7180
DOW

P. Muehlberg

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE

DATE THIS REPORT 6-12-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Water Samples - Saline Water Plant

DATE OF SAMPLE

Sample	Dow	Freeport
PPM Oxygen	Less than 1	Less than 1
pH	6.65	7.05
PPM CO_2	5	8
Chloride	7	22
Calcium	1	4

BY: RHD jsm

SIGNED R H Delaune

7180

DOW

P. E. Muehlberg (2)

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE XRD-803 and 804

DATE THIS REPORT 6-19-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Deposits from Coupons from Converted Water from the Freeport Saline Water Conversion Plant

DATE OF SAMPLE 6-11-64

Deposits from each of two coupons were examined by x-ray diffraction. The one coupon was from converted water to Freeport and the other from converted water to Dow. Both deposits showed to be essentially magnetite (Fe_3O_4). No other constituent was detected.

BY: K. C. Poulsen jsm

SIGNED K. C. Poulsen

7180
DOW

W. F. McIlhenny (2)

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE XRD-842

DATE THIS REPORT 7-10-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Sediment from O.S.W. of Freeport Water Filter

DATE OF SAMPLE 6-22-64

X-ray diffraction examination of this material showed the presence of magnetite (Fe_3O_4) as the minor constituent diluted by an amorphous constituent. The amorphous material is most likely hydrous iron oxide which tends to be amorphous.

BY: KCP

SIGNED K. C. Poulsen

7180

DOW

P. E. Muehlberg

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE B-205

DATE THIS REPORT 7-2-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Water Samples from Seawater Conversion Plant

DATE OF SAMPLE 6-22-64

Sample	PPM Oxygen
Seawater after acid mix	2.6
Seawater out	0.2
Raw seawater	1.2 and 2.75 (possibly sampled at wrong point?)
Vapor top	(a) Oxygen 8.1 PPM CO_2 57.2 PPM (b) Oxygen 4.8 PPM CO_2 66.3 PPM
Steam No. 11	Insufficient sample
Steam No. 2	Oxygen 20.1 PPM CO_2 3.8 PPM

BY:

SIGNED

7180

DOW

P. E. Muehlberg
R. Delaune

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE GC 823

DATE THIS REPORT 7-14-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Steam Samples from Saline Water Plant

DATE OF SAMPLE 6-30-64

Sample Desc.	Hydrogen	Oxygen	Mole % Nitrogen	Carbon Dioxide
Bomb No. 5	3.2	18.4	71.5	3.4
Bomb No. 2, Sample No. 1 - Vapor Steam from No. 1 Vapor body ahead of effect No. 2 heating element	18.5	8.6	51.7	22.0
Sample No. 3, Bomb No. 3 - Vent steam downstream of effect No. 3 heating elements. Cumulative non-condensibles from vapor bodies No. 1 and No. 2	0.4	1.0	5.2	88.1
Sample No. 2, Bomb No. 4 - down stream of heating element of No. 2 effect. Non-condensibles from vapor body of No. 1	1.3	13.0	51.8	32.9

Basis: GC

BY: TEG

SIGNED L B Wilkinson

7180

Paul Muehlberg

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE B-205

DATE THIS REPORT 7-20-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Samples Collected

DATE OF SAMPLE 6-25-65

Sample	Acidified Seawater	Seawater Out	Raw Seawater	Freeport Water	Dow Water	Saline Concentrate
PPM O_2	2.5	0.15	4.7	0.24	<0.1	11
PPM CO_2	52	8	---	13	4	6
PPM Cl	---	---	---	21	55	---
Hardness as PPM Ca	4.0	---	---	3	5	---
Methyl Orange Alkalinity as PPM $CaCO_3$	<5	<5	---	10	<5	10
pH in situ	4.15	6.40	---	7.30	8.32	----
pH in equilibrium with atmosphere	4.0	6.1	7.4	6.7	---	
PPM O_2 liquid	4	2.7	15.0	17.7	2.5	<1
PPM CO_2 liquid	36	405	180	29	8	4
M.O. alkalinity as $CaCO_3$ liquid	12	*	*	<5	5	6
PPM Sodium	---	---	---	8.6	---	---
pH in situ	---	---	---	---	6.80	8.05
pH in equilibrium with atmosphere	---	---	---	---	6.5	7.4

*Insufficient sample

BY:

SIGNED E. W. Nichols

7180

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE ____

DATE THIS REPORT ____

CHARGE ____

REPORT OF ANALYSIS

DESCRIPTION ____

DATE OF SAMPLE ____

Sample	Seawater Out	Dow Water	Freeport No.1	Freeport No. 2
Oxygen	10.7 PPM*	1.5	<1.0	1.6
CO_2	60 PPM*	3 PPM	7 PPM	8 PPM
Cl	--	49 PPM	120 PPM	120 PPM
Hardness as Calcium	--	2 "	3 "	3 "
pH "in situ"**	4.20	5.98	5.75	5.62
pH in equilibrium with atmos.	5.70	6.90	7.15	6.95

* Sample bottle probably leaked since these values seem unreasonably high.

**pH values "in situ" and pH values in equilibrium made at two different labs. Comparison of pH value of buffer will be made between labs and reported at a later date.

BY: BWN

SIGNED ____

7180

P. E. Muehlberg

THE DOW CHEMICAL COMPANY
TEXAS DIVISION

CENTRAL LABORATORY FREEPORT

FILE B-205

DATE THIS REPORT 7-20-64

CHARGE 7501-702

REPORT OF ANALYSIS

DESCRIPTION Samples Collected 6-29-64

DATE OF SAMPLE

	% O_2 Vapor	% N_2 Vapor	% CO_2 Vapor	Vol. Vapor	Vol. Liquid
Vapor from leaving No.1 effect	8.6	51.7	22.0	35 ml	470 ml
Vent stream from effects No. 1 and 2	1.0	5.2	88.1	135 ml	75 ml
Noncondensibles from vapor body No. 1 effect	13.0	51.8	32.9	80 ml	125 ml
Vapor from No.2 effect	18.4	71.5	3.4	35 ml	500 ml
Deaerator eff.	---	--	---	---	---
Brine from No. 1					

BY:

SIGNED E. W. Nichols

7180

DOW

THE DOW CHEMICAL COMPANY
TEXAS DIVISION
CENTRAL LABORATORY FREEPORT

P. E. Muehlberg

FILE

DATE THIS REPORT 7-30-64

CHARGE 1256-702-190

REPORT OF ANALYSIS

DESCRIPTION Water Sample - Effluent Brine from Deaerator at Saline Water Plant

DATE OF SAMPLE 7-30-64

PPM CO_2	6.6

BY: J. B. Hoot jsm

SIGNED E. K. Hill